PHOTOVOLTAIC EFFECT IN A COMPOSITE INVOLVING NONCONJUGATED CONDUCTIVE POLYMER AND C_{60}

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PHOTOVOLTAIC EFFECT IN A COMPOSITE INVOLVING NONCONJUGATED CONDUCTIVE POLYMER AND C_{60}

Aditya Kumar Palthi

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PHOTOVOLTAIC EFFECT IN A COMPOSITE INVOLVING NONCONJUGATED CONDUCTIVE POLYMER AND C_{60}

Aditya Kumar Palthi

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Date of Graduation

VITA

Aditya Kumar Palthi, son of Venkataramanaiah Palthi and Swaroopa Rani Palthi, was born on February 18, 1984 at Kamareddy, Andhra Pradesh, India. He graduated in 2005 with a Bachelor of Technology degree in Mechanical Engineering (Mechatronics) from Mahatma Gandhi Institute of Technology, Jawaharlal Nehru Technological University, Andhra Pradesh, India. In order to pursue higher education he came to Auburn University to join the M.S program in the Department of Mechanical Engineering.

THESIS ABSTRACT

PHOTOVOLTAIC EFFECT IN A COMPOSITE INVOLVING NONCONJUGATED CONDUCTIVE POLYMER AND C_{60}

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In this thesis, photovoltaic effect in a composite involving nonconjugated conducting polymer and C_{60} is reported. There has been an intensive research effort in the area of organic photovoltaic cells using conjugated polymers. Here, use of nonconjugated conductive polymers in the photovoltaic cells is being reported for the first time.

Composite involving a nonconjugated conductive polymer such as poly(β-pinene), cis-1,4-poly(isoprene) and SBR, and C_{60} was formed for use in a photovoltaic cell. The optical absorption and photoluminescence spectra of the films of these composites were studied. When the composites were formed, it was observed that the photoluminescence was totally quenched for the composite involving poly(β-pinene) and C_{60} and considerably decreased for the composite involving cis-1,4-poly(isoprene) and

C_{60}. The composite involving SBR and C_{60} did not show as much quenching of photoluminescence.

The photovoltaic cell was fabricated using ITO coated glass as one electrode and aluminum as the other, with a nonconjugated polymer-C_{60} composite film sandwiched between the electrodes. Nitrogen laser (325 nm) and illuminant white light bulbs (200-700nm) were used as the light sources and the photovoltage produced was recorded for different light intensities.

The composite involving poly(β-pinene) and C_{60} produced better photovoltaic characteristics when compared to the other composites. Among the composites formed by poly(β-pinene) and C_{60}, the one having 4% of C_{60} by weight showed the best performance. This can be attributed to the excellent homogeneity of the composite film at this concentration. The photovoltage produced for the composite involving poly(β-pinene) and 4% C_{60} by weight was linearly dependent on light intensity. About 280 mV was generated for an intensity of ~ 6mW/sq.cm. Pristine poly(β-pinene) has a photoluminescence peak at 360 nm for excitation at 280 nm. This photoluminescence is quenched when C_{60} is added to form the composite with poly(β-pinene). Therefore, the photovoltaic effect appears to be a result of excited state electron transfer from poly(β-pinene) to C_{60}.

The photovoltaic measurements of the composite involving poly(β-pinene) and C_{60} show that these are highly promising for application in low cost photodetectors and photo-sensors when compared to traditional photodetectors. Additional applications will include low cost solar cells.

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CHAPTER 1

INTRODUCTION

Energy is mainly divided into two types, nonrenewable energy and renewable energy. Nonrenewable energy is obtained from the nonrenewable sources which take a very long time to be formed. Once they are used it is very difficult to regain them. Fossil fuels fall under this category. Renewable energy is obtained from the renewable sources which can be recreated easily. Solar energy, hydro energy, wind energy, biofuels, geothermal energy, etc fall under this category. Energy can be converted into different forms depending on necessity using different technologies.

With the increase in the demand for energy and the depletion of nonrenewable sources of energy trend has been shifting towards the use of renewable sources of energy. The amount of energy needs met through renewable sources of energy is increasing at a good pace every year.

Solar energy is one of the most abundant forms of energy. It can be converted to either electrical energy or heat energy depending on the necessity. Photovoltaics technology is the area which deals with the conversion of light energy into electrical energy. It deals with transactions of electrons and holes between various materials. Solar

cells are the devices which convert the solar energy into electrical energy. These solar cells use either inorganic materials or organic materials for this conversion. The use of inorganic cells in solar cells started a long time back and extensive research has been done in this area and they have found their way into the commercial market. But, they had some disadvantages like very high installation costs, complicated fabrication process, etc. To overcome these disadvantages scientists have been working on various organic materials for their application in solar cells. So far a lot of research has been done on organic conjugated polymers for their use in solar cells. There is another class of polymers called the nonconjugated conducting polymers which has not been explored yet. Therefore, in this research an effort was made to study the characteristics of these polymers for their application in the photovoltaic cells.

In the chapter 2, a review of the world energy needs and the different sources of energy are discussed. A brief idea of the present world energy consumption and the projected needs is discussed. Statistics of the available nonrenewable sources of energy and the need for the use of renewable sources of energy are presented. Various renewable sources are briefly discussed. Emphasis is laid on the area of photovoltaics as the research here deals with photovoltaics. A brief history of research in the area of photovoltaics is given. The basic structure of a photovoltaic cell, various materials used in the photovoltaic cells and some breakthrough results has been discussed. The entry of organic polymers and the factors that led to this have been reviewed. Also an idea of various organic polymers used in the photovoltaic cells and some results obtained are given.

In chapter 3, the driving force behind the research and the main objectives of the research are discussed.

In chapter 4, the process of preparation of the composites involving the nonconjugated polymer and various concentrations of C_{60} by weight is described. Once the composite is formed, its optical properties are discussed. The absorption spectrum of the polymer and the composite are presented and the absorption peaks are discussed. The photoluminescence is studied and reason for the quenching of the photoluminescence in the composite is reported. The method of fabrication of the thin films of the composite and the study of the surface topography of the thin films is discussed. After the thin films are formed the components required for the experimental setup are given. The fabrication of the photovoltaic cell is described and the experimental setup is shown. The method of calibration of light intensity and obtaining the required data is described. Also, the experimental setup to study the current Vs Voltage characteristics is discussed.

Also in the same chapter, the photovoltage produced for a composite involving the nonconjugated conducting polymer, poly(β-pinene) and 4% C_{60} by weight at different intensities of light using a white light source is given. Also, the amount of Photovoltage produced for the composites having different concentrations of C_{60} (ranging from 2-8% by weight) at different intensities of incident light using a white light source is given. After this, the photovoltage produced for the composites having different concentrations of C_{60} (ranging from 2-8% by weight) at a fixed intensity of incident light of 2mW/sq.cm using Nitrogen Laser (325nm) is given. The reason for the better performance of the composite involving the nonconjugated conducting polymer, poly(β-pinene) and 4% C_{60} by weight over other composites is discussed. Also, the current-voltage characteristics of

the photovoltaic cell having the composite involving the nonconjugated conducting polymer, poly(β-pinene) and 8% C_{60} by weight are discussed. The SMU device is used to study these characteristics and the behavior of the cell in the light and dark condition is reported. After the reporting of all the results, a brief discussion of comparison of the organic photovoltaic cell using the nonconjugated polymer with the other solar cells using either inorganic or organic conjugated materials is given.

In chapter 5, all the properties discussed for poly(β-pinene) in chapter 4 are discussed for poly(isoprene).

In chapter 6, all the properties discussed for poly(β-pinene) in chapter 4 are discussed for SBR.

In chapter 7, a comparison of the materials is made based on the results.

In chapter 8, a brief summary of the whole research and the future work is given.

CHAPTER 2

BACKGROUND

2.1 INTRODUCTION

Energy drives the universe. We need energy to do anything and everything in our daily life. We are totally dependent on the supply of energy. The increase in world population is increasing the need for energy. It is estimated that the world population will be nearly doubled by the end of the twenty first century which will increase energy demand by nearly two fold. The world population statistics from 1950 and the projected population statistics till 2050 are shown below [1].

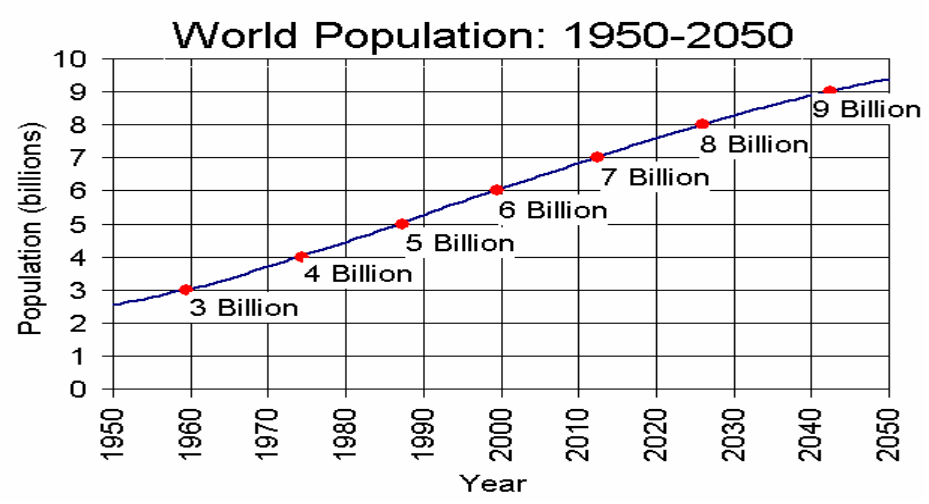


Figure 2.1 World Population statistics [1]

The population is projected to increase to 9 billion by 2042, which is nearly 50% increase from the year 1999 [1]. This would thereby cause an increase in the world energy consumption. The world energy consumption from 1980 and the projected energy consumption till 2030 is shown below [2, 3].

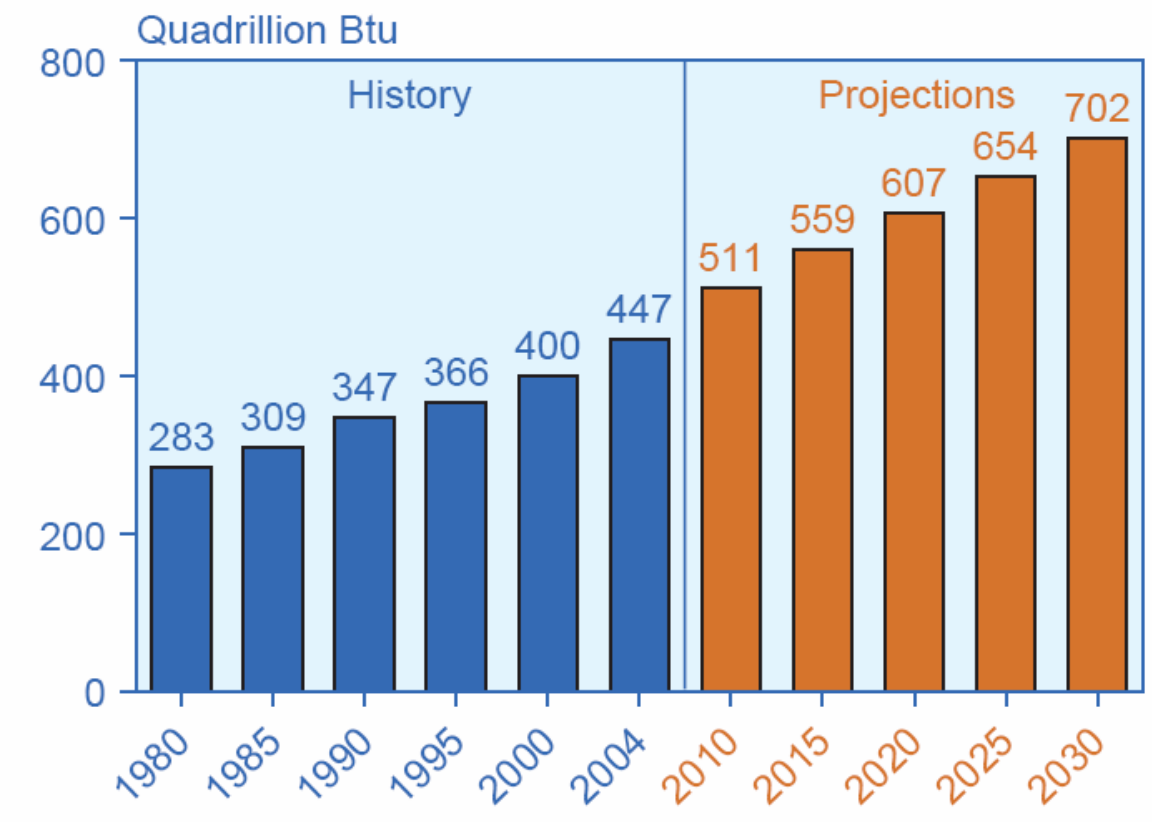


Figure 2.2 World Energy Consumption from 1980-2030 [2, 3]

It can be seen that by 2030 that world energy need is projected to go up by nearly 50% of present energy need. At present around 86.5% of the world energy needs are supplied through burning fossil fuels [4]. Trend has been shifting towards renewable sources of energy to counter the depleting supplies of nonrenewable sources of energy. In the following sections the types of energy sources will be discussed.

2.2 NONRENEWABLE SOURCES OF ENERGY

Nonrenewable sources of energy are those which are very hard to be recreated in a short period of time. They are divided into types, fossil fuels and nuclear energy.

2.2.1 FOSSIL FUELS

Oil, coal and natural gas fall under the category of fossil fuels. They cater to nearly 86.5% of world energy needs [4]. These are formed from the fossilized remains of animals and trees exposed to high temperatures and pressures over hundreds of millions of years. Studies show that 1 liter of gasoline is the time rendered result of around 23.5 metric tones of phytoplankton material deposited on the ocean floor [5].

Fossil fuels have played a major role in the industrial revolution. But with the increasing demand for energy, the fossil fuels are being depleted at a much faster rate than the rate at which they are being produced. The proven reserves of crude oil, coal and natural gas are shown below [6, 7].

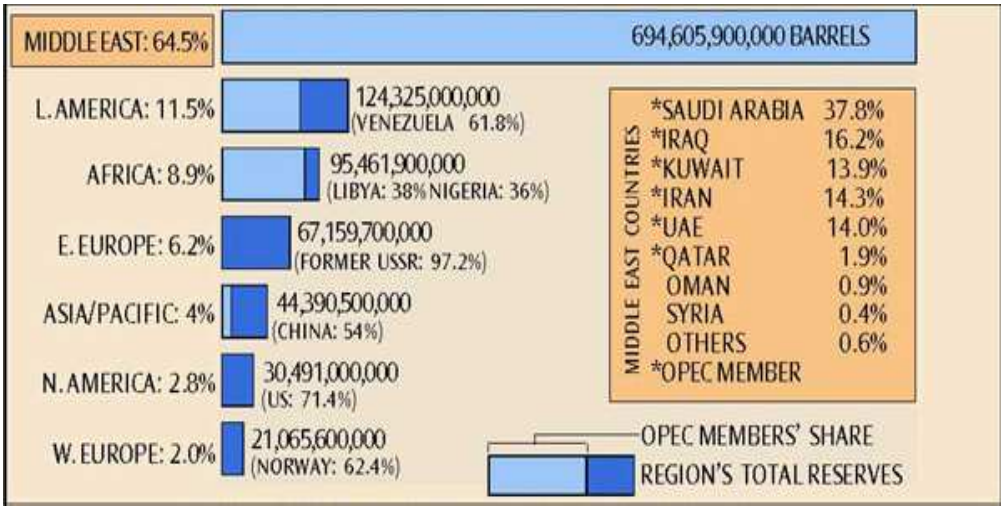


Figure 2.3 World proven crude oil reserves by region [6]

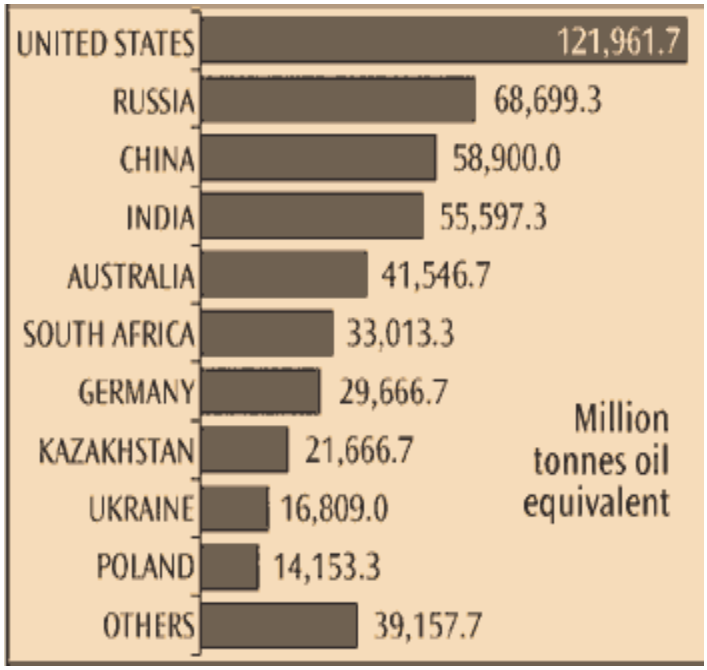


Figure 2.4 Proven coal reserves in top ten countries [7]

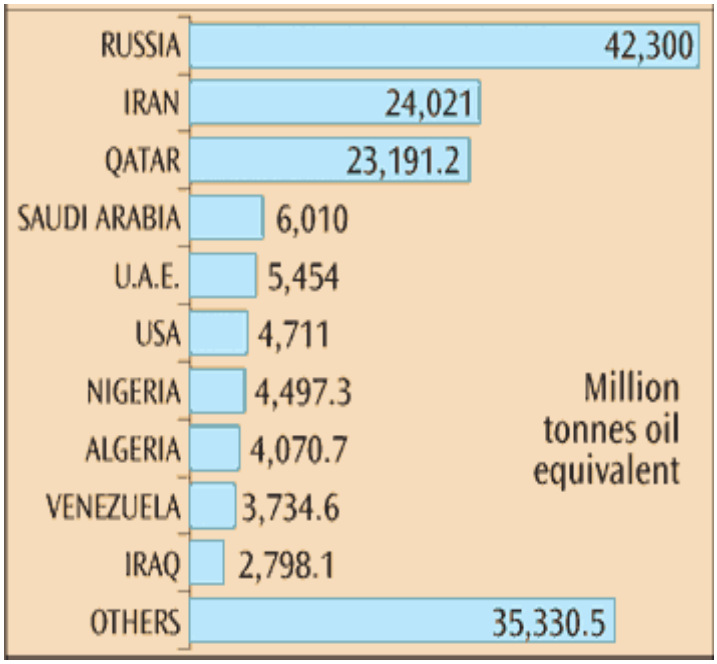


Figure 2.5 Proven natural gas reserves in top ten countries [7]

These reserves are being depleted at a very fast rate. Commercial use of petroleum started in the early nineteenth century [8]. Later, the production of oil has been increasing. It is predicted that the world's oil production is at its peak and would fall down 32% by 2020 [9]. The increased in demand for energy has lead to the rise of crude oil price from $18.91 per barrel in 1990 to $ 107.28 in April, 2008 [10]. The figure below shows the world major producers and consumers of oil [11].

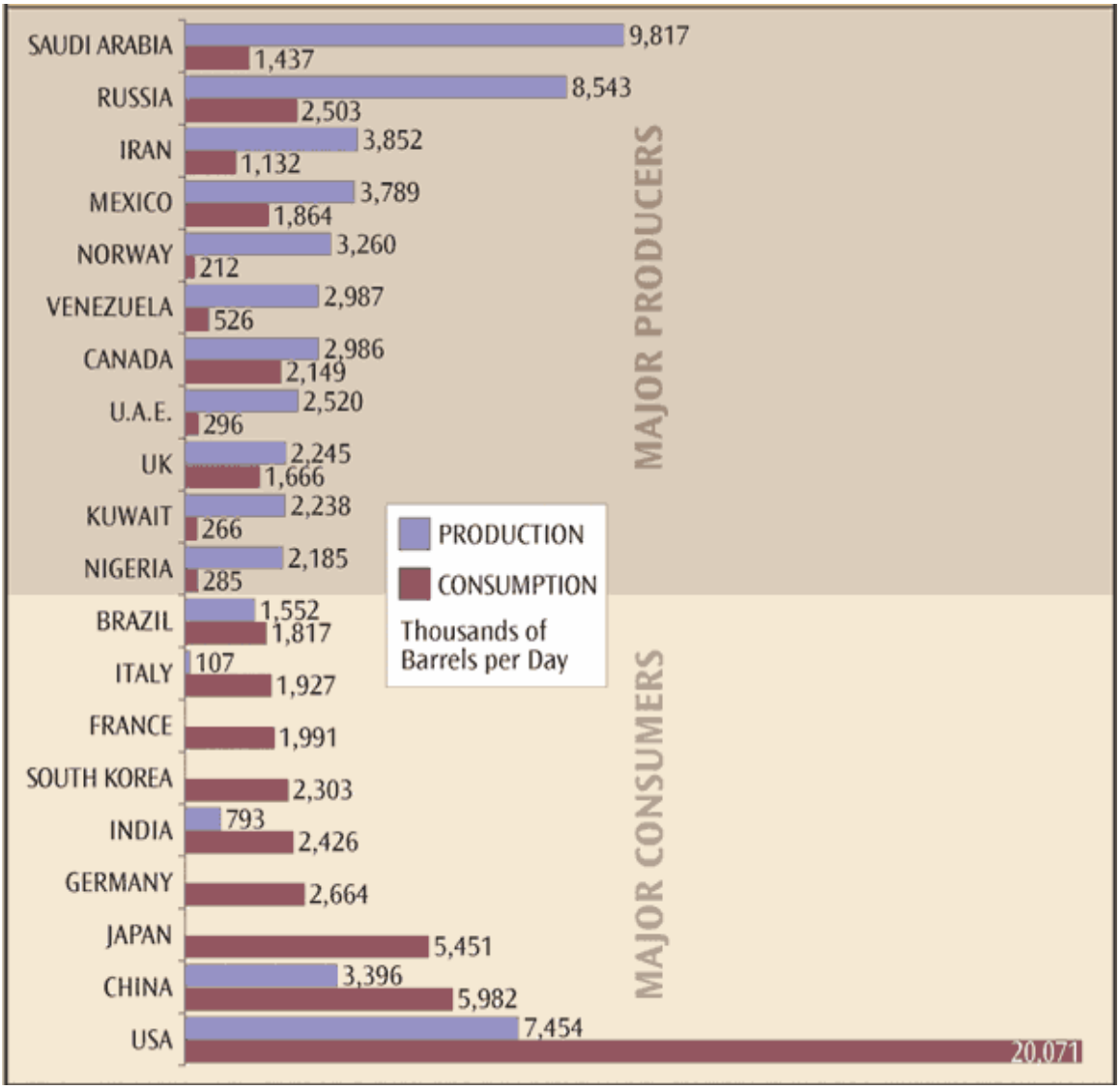


Figure 2.6 World's major producers and major consumers of oil [11]

If the use of oil continues at this pace the years of oil production left in the ground with the given reserves will soon be depleted.

Natural gas and coal reserves too are depleting fast. The figure below shows the world energy use by fuel [11].

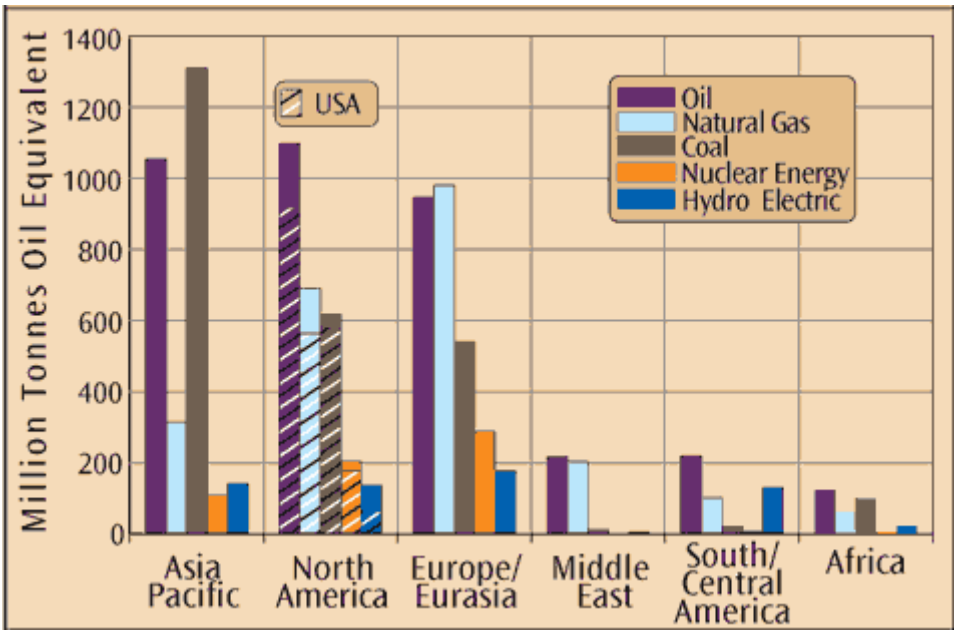


Figure 2.7 World Energy use by fuel [11]

It can be seen that the majority of the world energy use is from fossil fuels. One of the threats in using fossil fuels is that they emit CO_2 on combustion which is the major cause for global warming. The energy needs will be met using the fossil fuels in many years to come. If no action is taken and the trend continues, the CO_2 emissions are going to be doubled. In US, 90% of the greenhouse gases are due to the combustion of fossil fuels [12]. The global climate change caused by the greenhouse gas emissions is already showing its effect on ecosystem by causing additional 150,000 deaths per year [13]. Sulfuric, carbonic and nitric acids are generated upon combustion of fossil fuels leading to acid rains which have adverse effects on the ecosystem. Another adverse effect of

global warming is the melting of polar ice caps. Over the past century the average temperature of the air near the Earth's surface has gone up by around 0.74 degree Celsius [14]. If this process continues it could lead to the drastic changes in the climate and in the Earth's topography causing severe loss of life and property. In order to fight the global warming effects and reduce the greenhouse gases, governments are spending a lot of money to encourage research in the area of renewable sources of energy.

2.2.2 NUCLEAR ENERGY

The other nonrenewable source of energy is nuclear power. This is obtained from controlled nuclear reactions, either fission or fusion. Nuclear fission process is the widely used method for nuclear power generation. Enrico Fermi first achieved nuclear fission experimentally in 1934 when his team bombarded uranium with neutrons [15]. Nuclear power provided 6% of world's energy as of 2004 [16].

The main disadvantage of nuclear power is the radioactive waste which is very harmful. It is a great challenge to safely store and dispose the nuclear wastes. The most important nuclear waste is the spent fuel which comprises of unconverted uranium and significant levels of actinides (mostly plutonium and curium). The actinides are responsible for long term radioactivity [17]. Each year, 25 to 30 tonnes of spent fuel is produced by a large nuclear reactor [18]. These wastes, if not stored and disposed properly, can have adverse effects due to radioactive contamination. There have been many debates about the use of nuclear power to cater the energy needs because of the dangerous effects it can have.

As a result of all the above facts there has been a growing trend towards the use of renewable sources of energy.

2.3 RENEWABLE SOURCES OF ENERGY

Renewable sources of energy are those which can be recreated. Solar energy, wind energy, hydro energy, etc fall under this category. Recently, there has been a lot of attention towards the renewable sources of energy. The increase in demand for energy, the depletion of nonrenewable sources of energy, global warming effects caused by the combustion of fossil fuels are some of the reasons which diverted the attention towards the renewable sources of energy. There are many advantages in using renewable sources of energy. The main advantage is that they are sustainable and will never run out. Most of them are eco-friendly and do not emit greenhouse gases directly. They can help in controlling the global warming effect. They can also bring economic benefits to many regional areas.

The main resources of renewable energy are sunlight, wind, water and geothermal heat. The renewable technologies are solar energy, hydro power, wind power, geothermal energy and biofuels. Around 7% of the world energy needs were catered through renewable sources of energy in 2004 [19]. The following figure shows the world energy consumption from different sources [20, 21].

Majority of the world energy needs were met by fossil fuels. But the amount of energy contributed by the renewable sources of energy is increasing every year. A lot of new technologies to make use of renewable sources of energy are coming up.

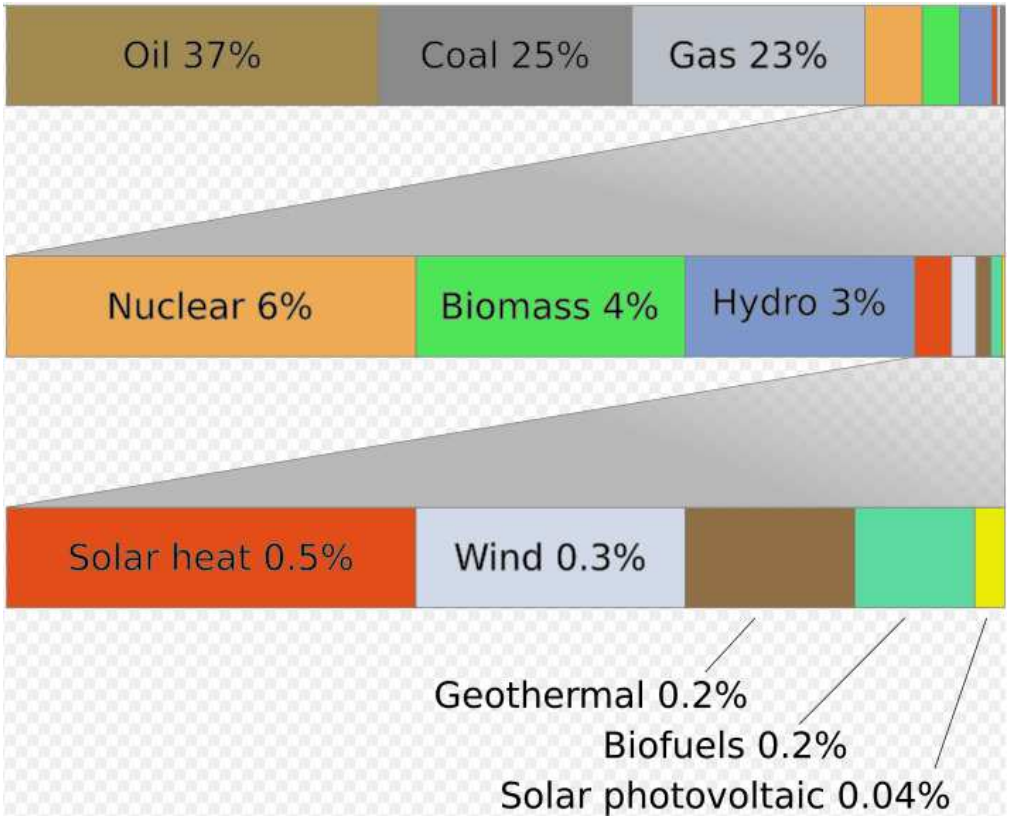


Figure 2.8 World energy consumption by energy source [20, 21]

It can be seen that the renewable energy was provided through biomass, hydro power, solar heat, wind, geothermal, biofuels and solar photovoltaics. Each of it is discussed below.

2.3.1 BIOMASS AND BIOFUELS

Biomass refers to the biological materials derived from recently living organisms like manure, garden waste, crop residue, etc. Biofuels can be produced from the recently dead living organisms most commonly plants. Biofuels are most commonly used as liquid fuels for automobiles. They can help to decrease the dependency on fossil fuels. They are highly dependable as they are obtained from renewable sources. But there are

various debates on using biofuels like deforestation, biofuels prices, carbon emissions, effect on food supply, etc.

2.3.2 HYDRO POWER

Most of the hydro power is generated from the potential energy of stored dam water. Large turbines are used to convert the potential energy to electricity. This is a very effective method as it does not involve any greenhouse gas emissions and produces no waste. It is also immune to the costs of fossil fuels as it does not need them for its production. The hydroelectric plants have longer life than the plants for fossil fuel generation. But, it has some disadvantages too. It can be disruptive to the surrounding aquatic ecosystem. As the normal flow of water is disrupted it can also lead to effects like soil erosion. In some cases canals are drawn to increase the head and avoid shallow parts of the river, which can at times cause the original river path to dry. This effects not only the aquatic life but also other animals like birds which breed along the river beds during particular seasons. Another effect is, construction of dams might require huge population relocation.

2.3.3 WIND ENERGY

Wind energy can be converted to other forms of energy such as electricity using equipment like the wind turbine. Use of windmills can be dated back to 1st century A.D [22]. Windmills were used extensively to grind flour [23]. They also contributed to the rail transport system expansion throughout the world by pumping water from wells necessary for the steam engines.

Conversion of wind energy to other forms of energy does not involve direst release of greenhouse gases. It reduces the use of fossil fuels. Some of the disadvantages are that the windmills can not be setup in urban areas because of the interference of the wind with the buildings. The amount of electricity produces through windmills varies as the wind speeds are not always constant.

2.3.4 GEOTHERMAL ENERGY

This refers to the energy generated from the heat stores beneath the surface of the Earth. The energy harnessed in clean and safe. It is very price competitive when compared to fossil fuels. A large geothermal plant can power an entire city. But it can have the disadvantage of effecting the surrounding environment around a geothermal plant. Dry steam involved in the geothermal plants also emits some greenhouse gases. But, they are negligible compared to the emission from a fossil fuel power plant.

2.3.5 SOLAR ENERGY

All the life on this Earth depends on the solar energy from sun. As the name says “Solar” energy, it is the energy that is obtained from the sun as radiation heat and light energy. The radiation heat from sun can be used to heat water and space, ventilation, cooking, heating swimming pools, industrial process, etc. The light energy from sun can be used and converted to electricity using appropriate devices. In the next section, photovoltaic technology will be discussed in detail.

2.4 PHOTOVOLTAICS

Photovoltaics is a technology which deals with the conversion of light energy into electrical energy. This is based on the photovoltaic effect which was first observed in 1839 by a French scientist, Henri Becquerel [24]. Some of the applications of photovoltaics are photodetectors like photosensors, photodiodes and photovoltaic cells for power generation.

2.4.1 PHOTODETECTORS

Photodetectors are the devices which are used to detect or sense light. Devices like photodiodes, photosensors, and phototransistors fall under this category. The photodetectors have a wide range of applications and are used widely as relays, switches, invisible perimeter security sensors, optical mouse, elevator door safety guards, toll gate automobile detection, optical tachometers, etc. These photodetectors use the basic principle of converting light to other forms like electrical signals (current or voltage). They are basically used as sensors or controls. In applications as sensors they produce an output signal depending on the light energy level it receives. Whereas in applications as controls, in addition to sensing light, a device provides controls capable of switching power to actuators that can control a process or a flow.

The present day photodetectors use inorganic semiconducting materials like silicon, germanium, cadmium sulphide, indium gallium arsenide, lead sulphide, etc. Depending on the band gap of the semiconductor used, a photodiode has the best detection ability at a specific range of wavelengths of light. These materials have disadvantages including intricacies in fabrication and high cost.

2.4.2 PHOTOVOLTAIC CELLS

The inorganic photovoltaic cells are configured as a pn junction. If the light striking the material has energy greater than the band gap of the material, electrons are excited to the conduction band from the valence band. The electrons and the holes move due to the electric field within the depletion region thereby creating a photovoltage or current. Whereas in organic photovoltaic cells, when light strikes the material, electrons are transferred from the polymer to the electron acceptor in the excited state and these electrons are carried to the lower work function electrode by the electron acceptor and the holes are carried to the higher work function electrode by the polymer creating a photovoltage or current.

There are many advantages of photovoltaics like [25]:

- Fuel source is very abundant
- Does not involve emissions and produces no wastes
- Low cost of operation
- No moving parts. Hence, no wear
- Operates in ambient temperature. No high temperatures involved
- Highly reliable
- Easy installation
- Environment friendly
- Require minimal maintenance
- Can be installed and operated in remote areas where fuel transport is difficult like satellites, islands, etc.
- Can be used in small, decentralized plants as well as large, central power plants

- Transmission and distribution losses can be reduced by using grid-connected solar electricity locally

It has some disadvantages like [25]:

- High cost of installation
- Produces DC and needs to be converted to AC
- Not available at night and in cloudy weather conditions. Therefore, storage or complimentary power system is needed

The disadvantages mostly relate to economics and infrastructure. They are compensated by very high public acceptance and environmental benefits.

The first functional photovoltaic cell was fabricated in 1883 by Fritts [26]. He used Selenium to fabricate the cell. The basic structure of a photovoltaic cell is as shown.

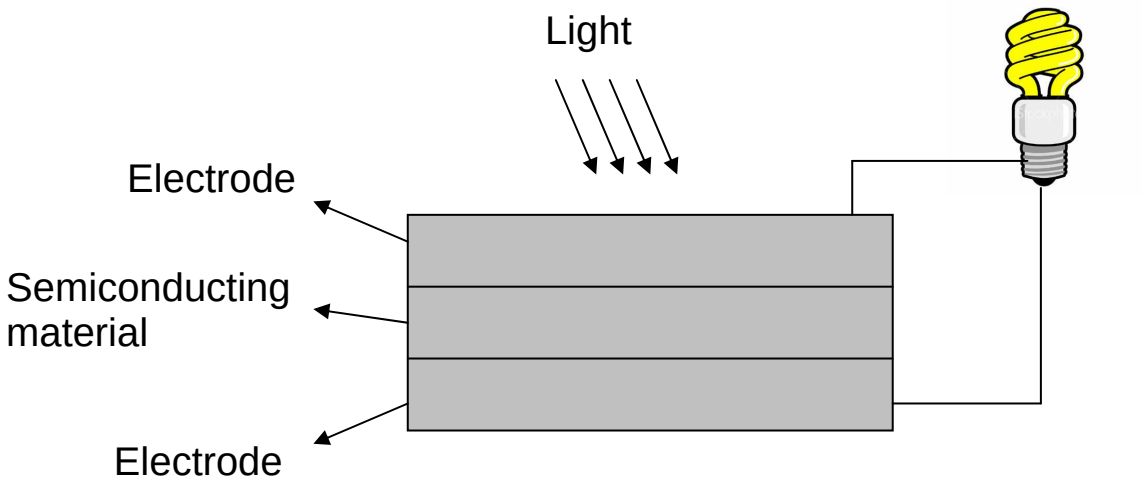


Figure 2.9 Basic photovoltaic cell

The Fritts cell consisted of thin layer of Selenium sandwiched between a very thin and semi-transparent gold layer and an iron layer. The gold layer acted as the high work function electrode and collected photo-generated positive charges, holes. The iron layer acted as the low work function material and collected photo-generated negative charges, electrons. When energy matched photon strikes selenium, a loosely bound electron-hole pair will be generated. The electron hole pair was separated and these free electrons and holes were called carriers. Theses carriers diffused to the respective and opposite electrodes driven by the two different work function metal electrodes [75].

The modern era of photovoltaics started when it was accidentally discovered in 1954 by a group of researchers in Bell Laboratories that pn junction diodes generated a voltage when the lights in the room were on [27]. Based on this discovery they produced a silicon pn junction solar cell with 6% efficiency [27, 28]. This had fuelled the research in the area of photovoltaics and led to the development of solar cells based on various semiconducting materials like Cu_2S/CdS, GaAs, CdTe, etc [29, 30, 31]. By 1960, several papers were published which developed the fundamentals of pn junction solar cell operation [27, 32-35]. In 1973, the world wide oil crisis spurred many nations to consider renewable sources of energy, which lead to the development of “violet cell” having an improved shorter wavelength response leading to 30% relative increase in efficiency over state-of-the-art Si cells [36]. From 1980s thin film solar cells came into play [25]. In 1985, Si solar cells with efficiency greater than 20% under standard sunlight [37] and greater than 25% under 200X concentration were produced [38]. The research in this area geared up and lot of books dedicated to photovoltaics were published and also universities offered degrees in the area of photovoltaics.

There has been a tremendous growth in the photovoltaics market in 1990s, nearly 33% per annum [25]. Solar photovoltaics provided around 0.04% of world's total primary energy supply in 2004 and estimated to increase to 0.4% by 2010 [39]. At first photovoltaics were used to power the satellites orbiting the earth. Later they have found their way in to the market and have a wide range of applications.

Most of the photovoltaic cells used thin films to obtain high efficiency. To obtain larger amount of power, the photovoltaic cells are connected in series to form a grid. Efforts are being made to further increase the efficiency of the cells.

Majority of the photovoltaic cells in the market use silicon. Due to the increase in demand for the photovoltaic cells, the price of Silicon has risen in the recent years. As the overall goal is the production of low cost photovoltaic systems, the main challenges of the present solar cell research are to [25]:

- Use lesser amount of semiconducting material by making thinner cells
- Use cheaper semiconducting materials
- Improve the performance using the cheaper semiconducting materials
- Increase material utilization by reducing the wastage of semiconducting material
- Increase the utilization of solar radiation by absorbing more spectrum efficiently
- Simplify the manufacturing process
- Reduce manufacturing and installation costs

To achieve this, one of the alternatives was to grow silicon ribbons [40, 41]. The growth of silicon ribbons does not involve expensive sawing process which is necessary to manufacture silicon wafers. However, the growth of silicon ribbons is a relatively slower process when compared to production of wafers.

Attention has been drawn to other semiconductors which could make good solar cells. Materials which existed in the form of thin films were considered. These materials had to be deposited on a substrate for mechanical support. To analyze the material properties, device structures and manufacturing issues unique to thin film solar cells a framework was developed as they differ considerably from silicon wafers [42]. Through 1970s, use of Cu_2S/CdS in solar cells lead to new theories that explained the device performance, new methods of material processing and new concepts in semiconductor device manufacturing [43, 44]. In 1981-1982, four thin film technologies, Cu_2S/CdS [45], a-Si [46], $CuInSe_2$/CdS [47] and CdTe/CdS [48], demonstrated the ability to cross 10% efficiency level and were seriously considered. Out of the four, Cu_2S/CdS was rejected due to stability problems related to electrochemical decomposition [49]. Lately, thin films of silicon are printed on aluminum for photovoltaic applications [50]. The main advantage of using thin films is that they can lower the cost of solar cells. But, the disadvantage is that their efficiency is lower and also they are much less understood compared to silicon wafer solar cells.

The other alternative which attracted a lot of attention was the use of organic conductive polymers which offered the ability to produce very thin photovoltaic cells. This will be discussed in the following section.

2.4.3 ORGANIC POLYMERS IN PHOTOVOLTAICS

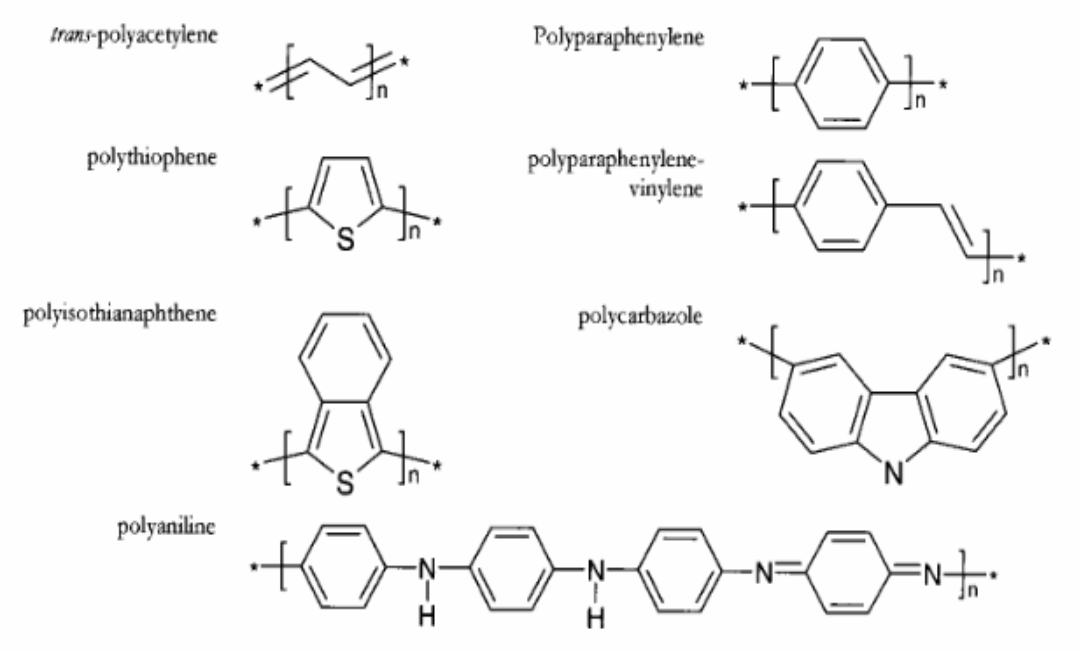
There has been significant research in the area of photovoltaics using organic conductive polymers. Conductive polymers are those having a special structure which becomes conductive upon doping with an electron acceptor. Some of the reasons which

attracted the attention towards the use of organic polymers in the photovoltaic/solar cells are [55]:

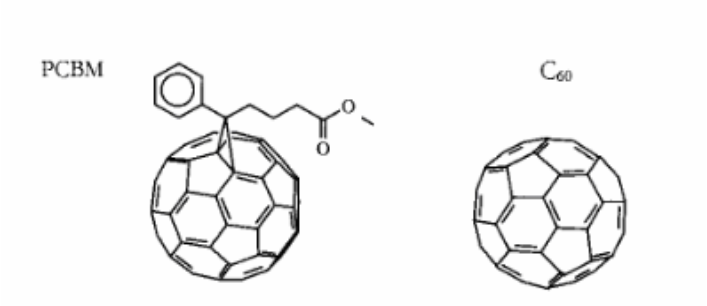
- Possibility of achieving extremely high optical absorption coefficient
- Can produce very thin solar cells which enable the use of a very small amount of the material
- Can produce large area solar cells which is a major drawback in inorganic solar cells
- Ease of fabrication
- Less maintenance
- Very cheap when compared to the traditional solar cells
- Involves low temperature processes in manufacturing when compared to that of inorganic solar cells

Research on organic photovoltaic cells began in 1950s. The first two layer organic photovoltaic system appears to have been reported in 1958 [56]. A variety of materials and compositions have been investigated for use in solar cells. Compounds such as merocynanines [57] and phthalocyanine [58] deposited as thin films by vacuum evaporation showed efficiency of about 1% for small sized photovoltaic elements. Composites involving an organic polymer and an electron acceptor like C_{60} and its derivatives have been used in photovoltaic cells. Buckminsterfullerene, C_{60} and its derivatives had been widely used in the area of photovoltaics since its discovery [59]. A two layer thin film photovoltaic cell exhibiting reasonable power conversion efficiency was fabricated by Tang using copper phthalocyanine and a perylene tetracarboxylic derivative [60]. It has been reported that organic solar cells can achieve an efficiency of

nearly 5% [77, 78, 79, 80]. Poly(p-phenylene vinylene) (PPV) has been widely used in the area of organic photovoltaic devices [61]. PPV-based devices were studied by groups at University of Cambridge, UK [62] and University of California, Santa Barbara [63]. Reports have been made on photovoltaic devices based on polythiopene [64-66].



(a)



(b)

Figure 2.10 Some of the widely used (a) conjugated polymers and (b) electron acceptors [74]

In 1992, a strong photoinduced electron transfer between C_{60} and a conjugated polymer MEH-PPV was reported by Sariciftci *et al.* [67]. Also work performed by Morita *et al.* showed evidence of photo-induced charge transfer in other polymer-fullerene composites [68, 69].

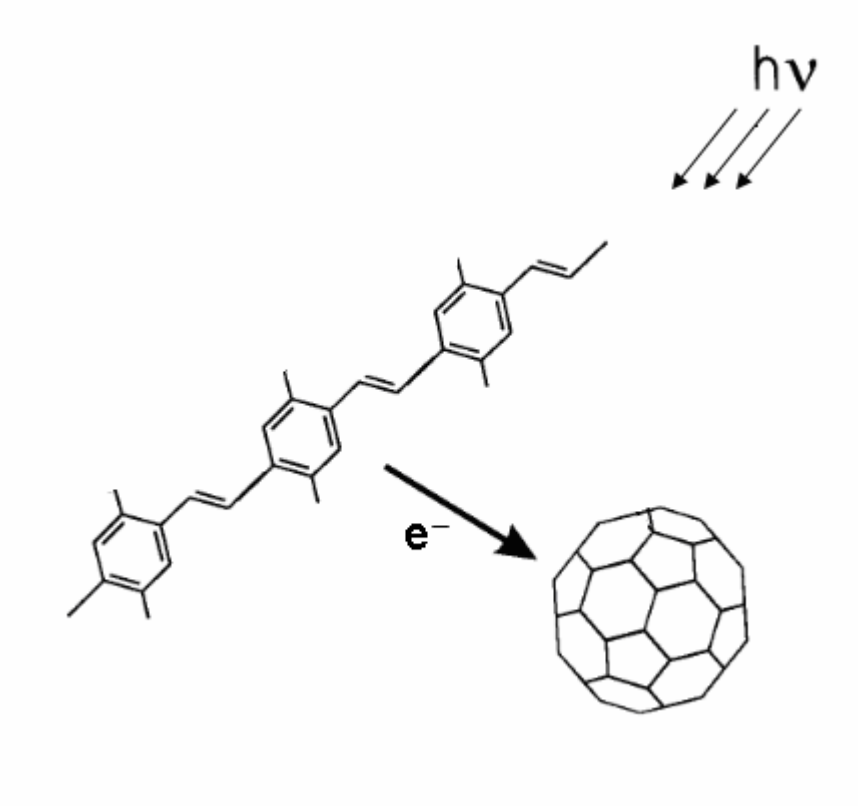


Figure 2.11 Schematic of photoinduced electron transfer between a conjugated polymer and fullerene [74]

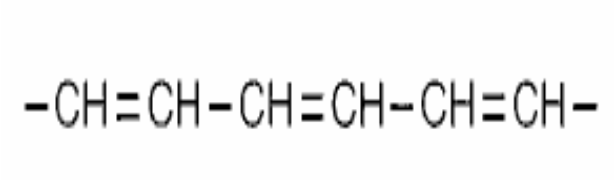
The organic photovoltaic cells show very promising results and can serve as low cost alternatives to the inorganic photovoltaics [70-72].

The organic polymers are used in the photovoltaic cells were conjugated polymers. So far, there has been no report of using nonconjugated conductive polymers

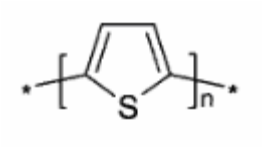
in photovoltaic cells. The conjugated and nonconjugated conductive polymers are discussed briefly in the following section.

2.4.3.1 CONJUGATED CONDUCTIVE POLYMERS

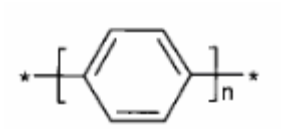
Conjugated polymers are those which have a framework of alternate single and double bonds in their repeat units. These polymers become electrically conductive upon doping with an electron acceptor [51]. One of the examples for a conjugated polymer is polyacetylene. Its structure is as shown.



Polyacetylene



Polythiophene



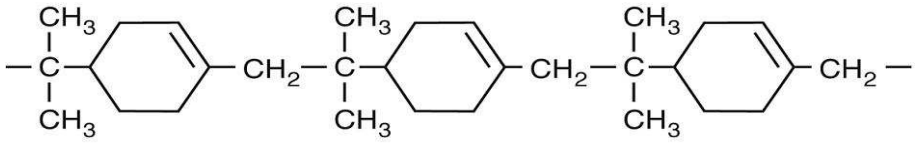
Polyparaphenylene

Figure 2.12 Structures of some conjugated polymers

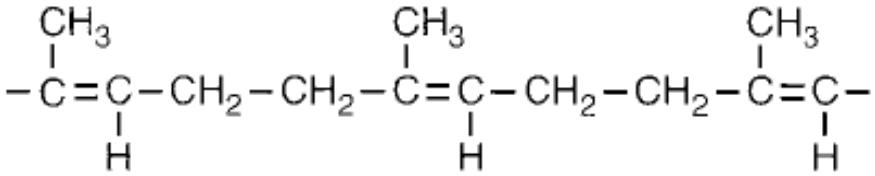
The single bonds in the structure are referred to as σ (Sigma)-bonds and the double bonds consist of σ and π (pi) bonds. The σ –bonds are formed from overlapping of sp^2 hybrid orbitals. The remaining out-of-plane p_z orbitals on the carbon atoms overlap with neighboring p_z orbitals to give π-bonds. The π bonds are the weaker bonds and responsible for the conductive nature of the polymer.

2.4.3.2 NONCONJUGATED CONDUCTIVE POLYMERS

Nonconjugated polymers are those which have at least one double bond in their repeat units. It was first believed that conjugation was a necessity for the polymer to be conductive. In 1988, this myth was broken after an intensive research was carried out by Mrinal Thakur to prove that conjugation was not a necessity for the polymer to be conductive. It was proved by him that the nonconjugated polymers could become conductive upon doping with suitable dopants [52, 53]. Conjugated conductive polymers are a subset of nonconjugated conductive polymers. Cis-1,4-polyisoprene is one such nonconjugated polymer which becomes electrically conductive upon doping with an electron acceptor [54]. Many other polymers with nonconjugated backbone like 1, 4 polybutadiene**,** polyalloocimine and poly(β-pinene) were studied for their optical and electrical properties. The structures of poly(β-pinene) and cis-1,4-poly(isoprene) are as shown.



(a)



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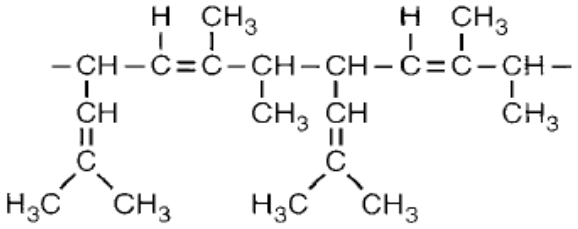
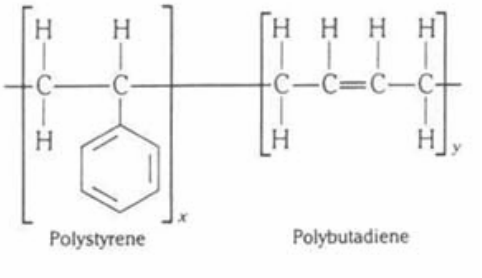


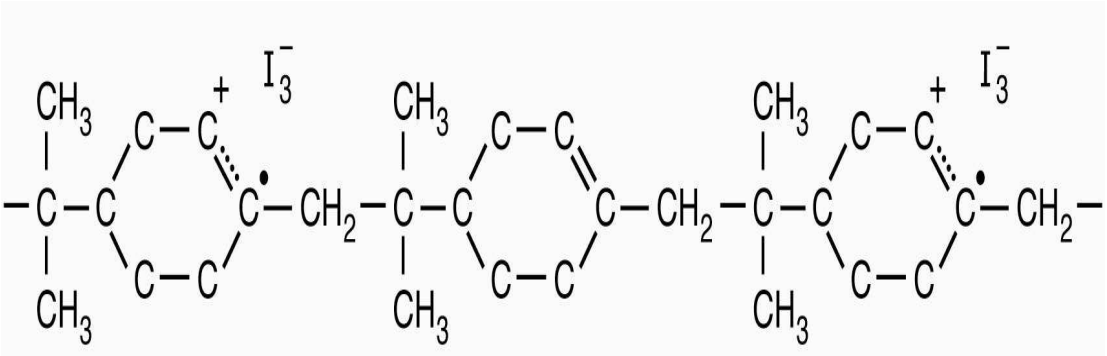


(c) (d)

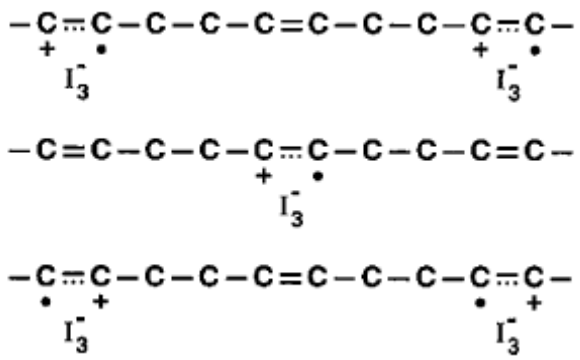
Figure 2.13 Structure of (a) poly(β-pinene) (b) cis-1,4-poly(isoprene)

(c) Poly(alloocimene) (d) Styrene-butadiene rubber (SBR)

These polymers become electrically conductive when doped with an electron acceptor like iodine [73]. The electrical conductivity of the polymer goes up in ten orders of magnitude upon doping it with iodine. The structure of the polymer upon doping with iodine is as shown below.



(a)



(b)

Figure 2.14 (a) Doped poly(β-pinene) and (b) cis-1,4-poly(isoprene)

showing the radical cations

It can be seen that radical cations are formed upon doping it with an electron acceptor like iodine and it becomes electrically conductive.

There has been a lot of research in the area of organic photovoltaics using conjugated polymer. Nonconjugated conducting polymers are a new class of polymers which can be explored for their application in the area of photovoltaics. Therefore, an effort has been made to study the photovoltaic characteristics of the nonconjugated conducting polymers and the photovoltaic effect in a composite involving a nonconjugated conducting polymer and fullerene will be discussed for the first time.

CHAPTER 3

OBJECTIVES

Photovoltaics is one of the areas which can cater to the increasing demand of energy. In 2004, only 0.04% of world energy needs was supplied through photovoltaics [39]. Solar energy is the most abundantly available renewable energy source. An attempt to tap this energy and convert it to photovoltage using technology involving ease and low cost has been the driving force behind the research carried out here. Also, to demonstrate low cost photodetectors, photosensors using novel polymer composites has been the other motivation.

There has been a lot of research in the area of photovoltaics using *conjugated* conducting polymers (composites involving a conjugated conductive polymer and C_{60}). The aim of the research is to develop a photovoltaic cell using a *nonconjugated* conductive polymer for the first time. Nonconjugated conducting polymers have at least one double bond in their repeat unit (double-bond number fraction less than ½) and become electrically conductive upon doping with an electron acceptor. This charge-transfer characteristic of the nonconjugated conductive polymers enables their application in the area of photovoltaics.

The specific objectives of the research are

- To form a composite involving a nonconjugated conductive polymer and buckminsterfullerene, C_{60} for use in a photovoltaic cell
- To fabricate thin films of these composites
- To measure and analyze the optical absorption characteristics for different compositions of these composites
- To measure and analyze the photoluminescence characteristics for different compositions of these composites
- To fabricate a photovoltaic cell using these thin films of the composites involving nonconjugated conducting polymer and buckminsterfullerene, C_{60}
- To analyze the photo-voltaic characteristics of these photovoltaic cells
- To analyze the dependence of the photovoltage produced on the intensity of the light source used
- To analyze the dependence of the photovoltage produced on the concentration of C_{60} present in the composite film involving poly(β-pinene) and C_{60}
- To analyze the photovoltaic characteristics for other nonconjugated conducting polymers such as cis-1,4-poly(isoprene) and styrene-butadiene rubber (SBR)
- To compare results, device characteristics and to draw conclusion

CHAPTER 4

THE PHOTOVOLTAIC EFFECT IN COMPOSITE INVOLVING A NONCONJUGATED CONDUCTING POLYMER, POLY(β-PINENE) AND BUCKMINSTERFULLERENE, C_{60}

4.1 INTRODUCTION

During the past few decades there has been a lot of research in the area of solar cells using organic polymers. The organic solar cells offered some advantages over the inorganic solar cells like low cost, greater area, flexibility, etc. All the research was concentrated in using conjugated polymers in the solar cells. There were no reports of nonconjugated conducting polymers being used in solar cells. Considering this an effort has been made to study the photovoltaic properties of the composites involving nonconjugated conducting polymers and C_{60} for their application in solar cells.

4.2 PREPARATION OF THE COMPOSITE INVOLVING A NONCONJUGATED CONDUCTING POLYMER, POLY(β-PINENE) AND C_{60}

The composite was formed by using Toluene as the base solvent. Weighed quantities of poly(β-pinene) and C_{60} were taken and added to it and let to dissolve to form

the composite. Composites having different concentrations of poly(β-pinene) and C_{60} were prepared. Typically, the amount of C_{60} was measured as % by weight in the composite. The following table shows the composites having different concentrations of C_{60} ranging from 0-8% by weight.

Sample	**% of C_{60} by weight in the composite**
Sample 1	8%
Sample 2	6%
Sample 3	4%
Sample 4	2%
Sample 5	1%

Table 4.1 Composites with poly(β-pinene) and different concentrations of C_{60}

Once the composites were prepared they were heat treated to enhance the solubility of the solutes. The following figure shows the color of the solution of the composites with different concentrations of C_{60}.

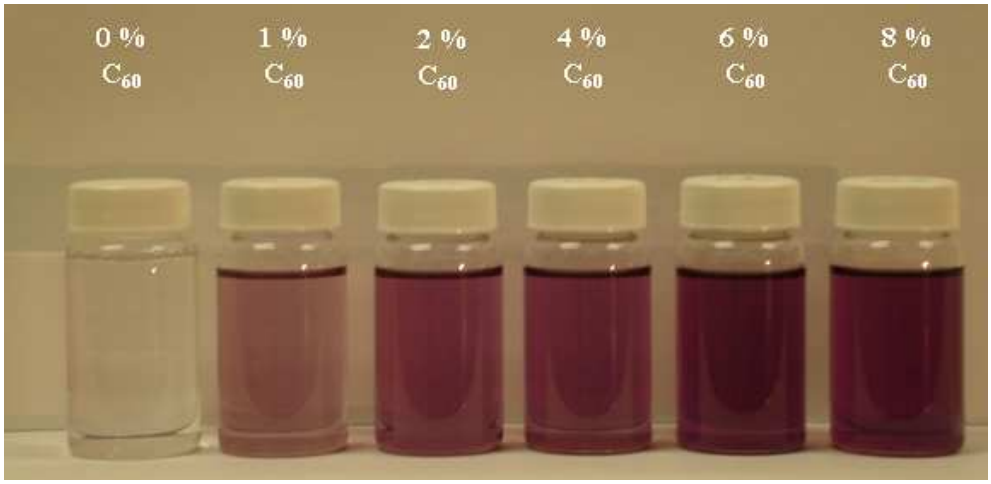


Figure 4.1 Solutions of the composites with different concentrations of C_{60}

The color of the composite solution intensifies with the increase in the concentration of C_{60}. Upon the formation of the composites, their optical properties, absorption spectrum and photoluminescence, were studied.

4.3 ABSORPTION SPECTRUM

Films of the composites were formed and the absorption spectra of these films were studied. Pristine poly(β-pinene) has an absorption peak at 280nm [73]. The optical absorption spectra of the composites formed by poly(β-pinene) and C_{60} at different concentrations is shown in figure . The inset in following figure shows the absorption spectrum of C_{60}.

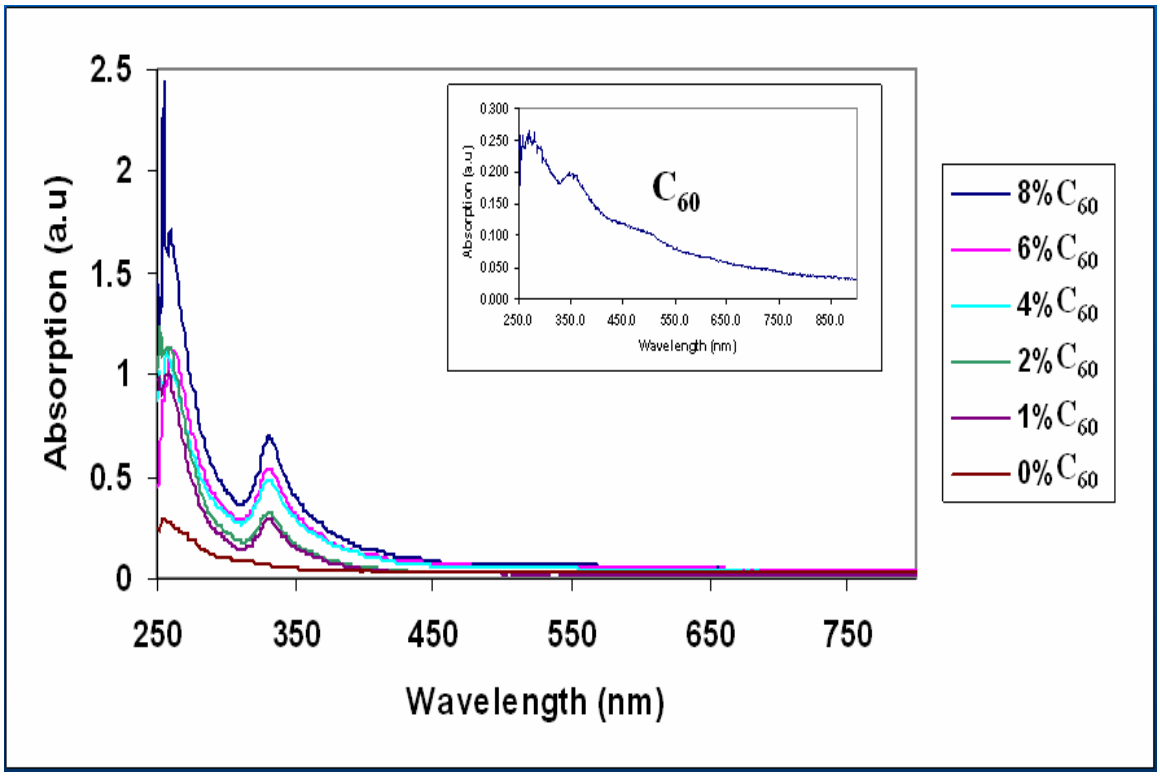


Figure 4.2 Absorption Spectra of the composites involving Poly(β-pinene) and C_{60} (% weight)

The absorption spectra of the composites show two distinct peaks, one at 280nm and the other at 335 nm. The peak at 280 nm observed in the composite is due to poly(β-pinene) and C_{60}, while the peak at 335nm is due to C_{60} alone. The intensity of the absorption peak for the composite film increases with increase in the concentration of C_{60} (by % weight). In the figure, the bottom most spectrum corresponds to the composite with 0% C_{60} by weight (pristine poly(β-pinene)). The spectrum above it corresponds to the composite having 1% C_{60} by weight. The top most spectrum corresponds to the composite having 8% C_{60} by weight.

4.4 PHOTOLUMINESCENCE

The photoluminescence of the composite films has been studied using Perkin Elmer LS-55 spectrometer. Pristine poly(β-pinene) has an emission peak at 360nm for an excitation wavelength of 280nm [73]. This is seen in the figure below.

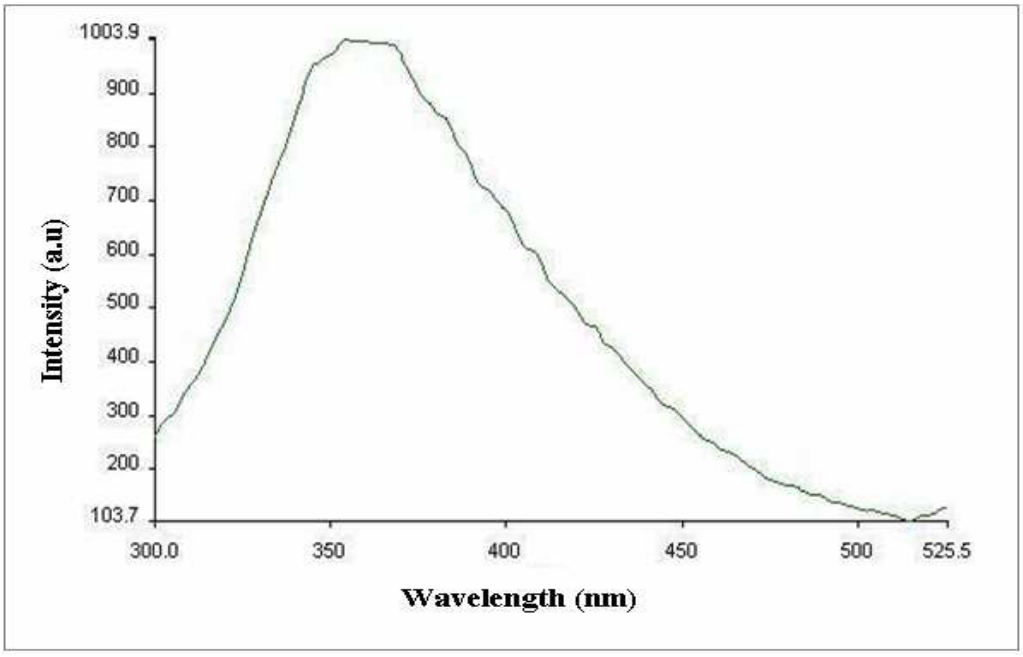


Figure 4.3 Photoluminescence spectrum of pristine poly(β-pinene)

The photoluminescence is quenched in the composite involving poly(β-pinene) and C_{60} due to the transfer of electron from the polymer, poly(β-pinene) to C_{60} in the excited state. It can be observed from the figure that there is no photoluminescence for the composite involving poly(β-pinene) and C_{60} at the same excitation wavelengths.

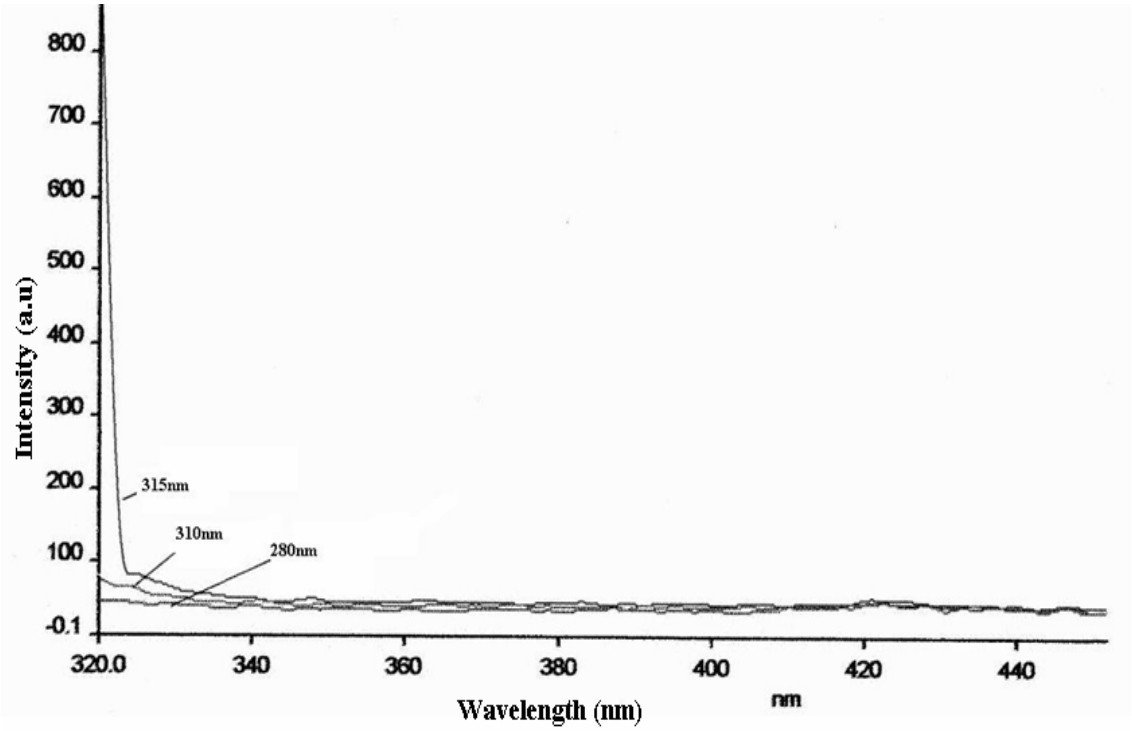
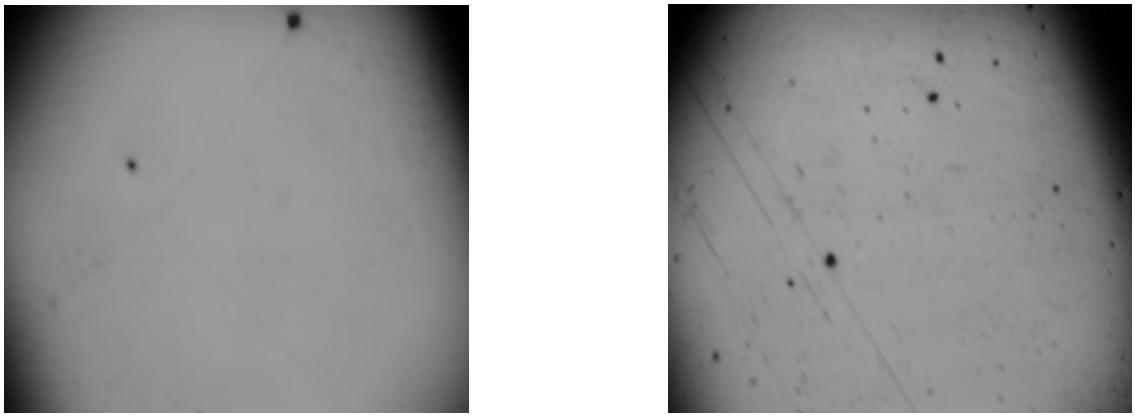


Figure 4.4 Photoluminescence of the composites involving Poly(β-pinene) and C_{60}

4.5 PREPARATION OF THIN FULMS OF THE COMPOSITES

Thin films of the composites involving the nonconjugated conductive polymer, poly(β-pinene) and C_{60} were cast on a glass slide. This was done by taking a few drops of the solution of the composite in a pipette and putting it on a glass slide. It is then allowed

to dry under normal environmental conditions. The following figure shows the optical micrographs of these films.



Composite with 4% C_{60} Composite with 8% C_{60}

Figure 4.5 Optical micrographs of the composite films involving Poly(β-pinene) and C_{60}

It was observed that the composite film having 4% C_{60} by weight was more homogeneous compared to the film having 8% C_{60} by weight. This is because the solution is saturated when the C_{60} is about 4% by weight.

4.6 PREPARATION OF ELECTRODES

The electrodes used in the experiment were Indium tin oxide coated glass slide and Aluminum coated glass slide. The Indium tin oxide glass slides with specifications of 4-8Ω resistance were ordered from a vendor. The aluminum coated glass slides were prepared in the Photonic Materials Research Laboratory using the Vacuum Evaporator.

4.7 LIGHT SOURCE

The light source used in the experiment was a white light bulb manufactured by GE, Inc. The wavelength spectrum of the light source is as shown below which was measured by Ocean Optics Spectrometer USB2000. The intensity of the light was measured using Newport Optical Power meter, model 1830-C.

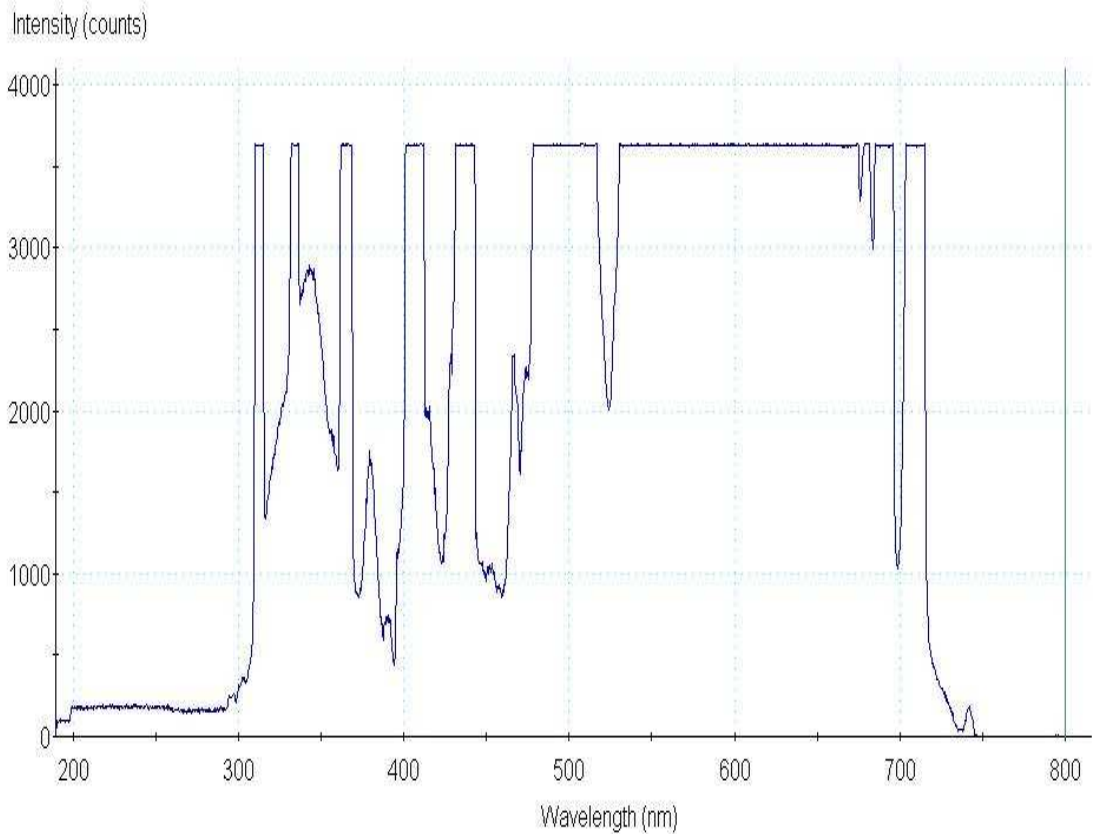


Figure 4.6 Wavelength spectrum of the light source

4.8 ELECTROMETER

The electrical measurements were made using a high impedance electrometer manufactured by Keithley Instruments (Model: Keithley 617 Programmable Electrometer).

4.9 EXPERIMENTAL SETUP

Photovoltaic cells used in the research were formed by sandwiching the composite film between two electrodes. Aluminum coated glass slide was used as one electrode and indium tin oxide coated glass slide was used as the other electrode. The Aluminum electrode was prepared by evaporating aluminum on a glass slide using the Vacuum Evaporator. The experimental setup is shown in figure.

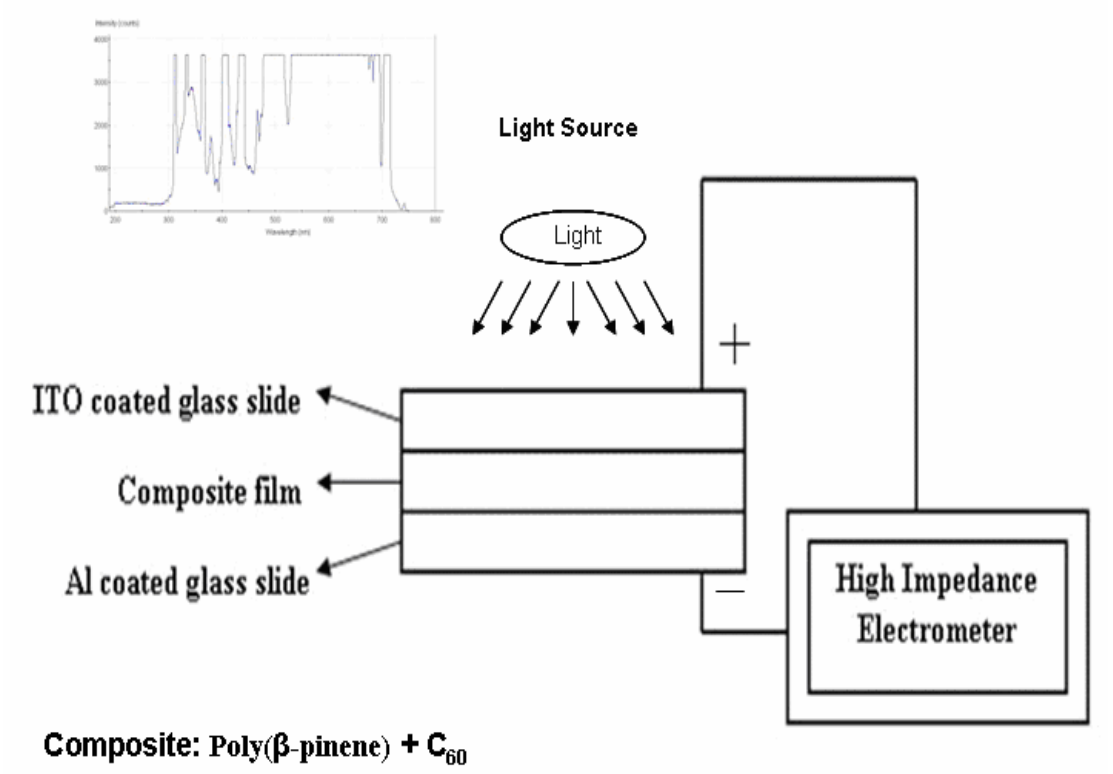


Figure 4.7 Experimental setup to measure the photovoltage for the composite involving poly(β-pinene) and C_{60}

The film of the composite involving poly(β-pinene) and C_{60} was cast on the aluminum electrode and the indium tin oxide electrode was placed on it. Pressure was applied to keep the composite and the electrodes in contact. Al foil was wrapped around the aluminum electrode at one corner and was connected to the negative terminal of a

high impedance electrometer (Keithley 617 Programmable Electrometer) using crocodile clip and the indium tin oxide electrode was connected to the positive end of the high impedance electrometer. The Indium tin oxide electrode was placed facing up to ensure that the light is incident on the polymer through this electrode.

The inset in the figure shows the wavelength spectrum of the white light source used in these measurements. The intensity of the incident light is calibrated in terms of the distance of the light source from the photovoltaic cell. The distance of the light source is changed to change the intensity of the incident light.

The above setup was used to make the photovoltage measurements. The following setup was used to make the Voltage versus Current measurements.

A device called Stimulus Measuring Unit (SMU) was used to study the dependence of current produced on voltage supplied. The cell was connected to the SMU and the SMU was interfaced with the computer as shown in the figure.

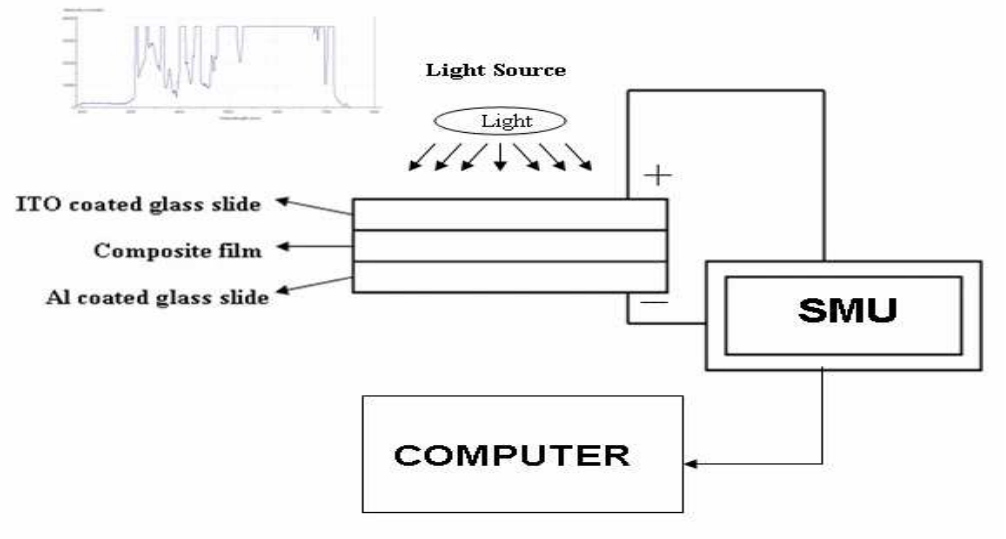


Figure 4.8 Experimental setup to study the Current Vs Voltage characteristics for the composite involving poly(β-pinene) and C_{60}

The Voltage range is given to the SMU through the computer and the SMU supplies the voltage to the cell in steps and takes the corresponding current output and gives it to the computer.

4.10 EXPERIMENT

The sample was set on a horizontal surface and connected to the high impedance electrometer using crocodile clips. The light source was placed in such a way that the light was incident directly on the composite film through the tin oxide electrode. The distance of the light source from the sample was calibrated in terms of intensity of incident light using a power meter. Therefore by changing the distance of the light source from the sample the intensity of incident light can be changed.

Before the start of the experiment the cell was discharged for one full night to make it free of residual charges. This is done by placing the sample in short circuit connection i.e., connecting the Al electrode and the Indium Tin Oxide electrode using a crocodile clip.

Once the setup was ready the electrometer was turned ON and it was made sure that the cell did not short. This was done by setting the electrometer in resistance mode and making sure that it showed high resistance (usually in Giga-ohms). If the cell showed high resistance, the electrometer was changed to voltage mode and the initial voltage was recorded after the reading was stable. The light source was then turned ON and the voltage reading in the electrometer was recorded. The difference in the voltage readings of the electrometer, with the light turned OFF and light turned ON, gives the amount of photovoltage produced at that particular intensity of incident light.

After this, the distance of the light source from the sample was changed to set it at a different intensity level and the experiment was repeated again. In this way the amount of photovoltage produced was recorded for different intensities of incident light source.

4.11 RESULTS

The photovoltage produced by the photovoltaic cell using the composite involving the nonconjugated polymer, poly(β-pinene) and C_{60} was recorded under different conditions as follows:

1. Photovoltage produced for a composite involving poly(β-pinene) and 4% C_{60} at different intensities of the incident light
2. Photovoltage produced for the composites having different concentrations of C_{60} (ranging from 2-8% by weight) at different intensities of incident light
3. Photovoltage produced for the composites having different concentrations of C_{60} using Nitrogen Laser (325nm) with a fixed incident light intensity of 2mW/sq.cm

Also, the I-V characteristics were recorded for the composite involving poly(β-pinene) and 8% C_{60}. All the results are shown in the following sections.

4.11.1 PHOTOVOLTAGE PRODUCED FOR A COMPOSITE INVOLVING POLY(B-PINENE) AND 4% C_{60} AT DIFFERENT INTENSITIES OF THE INCIDENT LIGHT

The photovoltage produced for a composite involving the nonconjugated polymer, poly(β-pinene) and 4% C_{60} by weight was recorded for different intensities of the incident light. White light source with a wavelength range of 300-700nm was used.

The following table shows the photovoltage produced for different intensities of incident light.

Intensity of incident light (mW/Sq.cm)	Photovoltage (mV)
3.5	162
6	280
9	430
12	550

Table 4.2 The photovoltage produced for different intensity of light for a composite involving poly(β-pinene) and 4% C_{60} by weight

It was observed that the photovoltage produced increased with increase in the intensity of the incident light as shown in the figure. A light intensity of 6mw/sq.cm yielded a photovoltage of 280mV. The results were plotted in a graph and it was observed that the photovoltage produced was linearly dependent on the intensity of light incident as shown in the following figure.

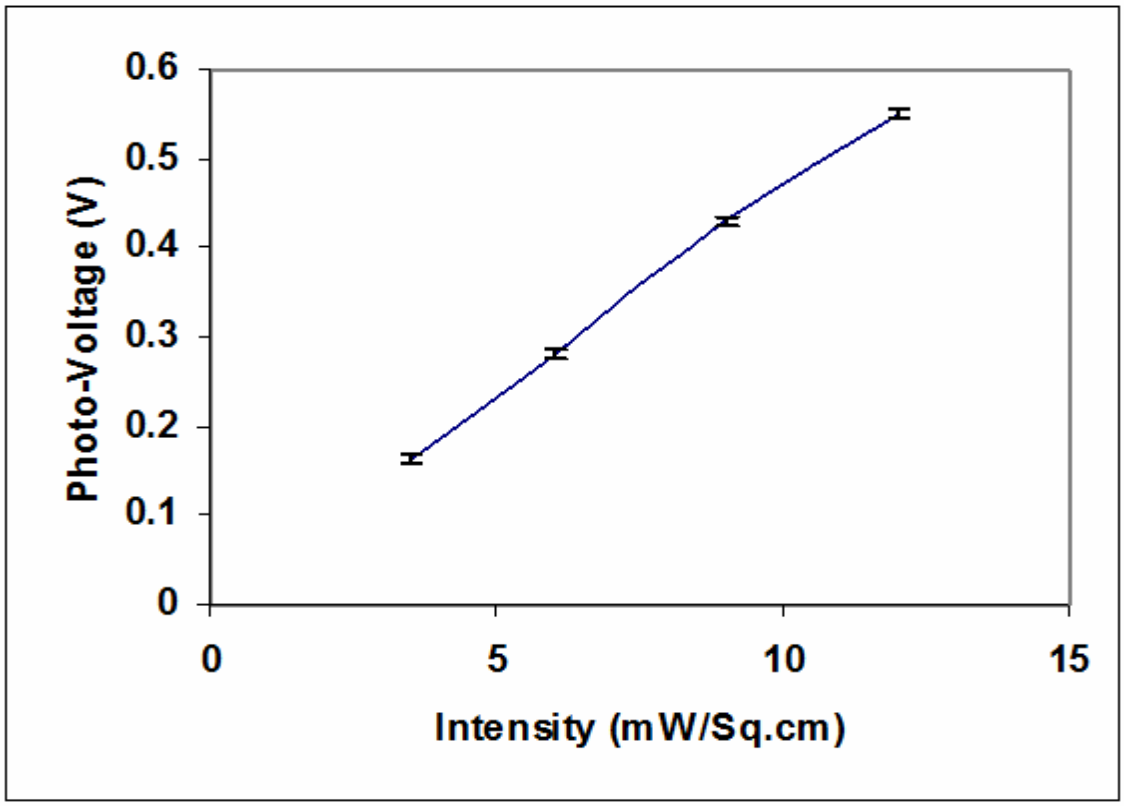


Figure 4.9 Photovoltage (Vs) Incident light intensity for a composite containing poly(β-pinene) and 4% C_{60} by weight

4.11.2 PHOTOVOLTAGE PRODUCED FOR THE COMPOSITES HAVING DIFFERENT CONCENTRATIONS OF C_{60} AT DIFFERENT INTENSITIES OF INCIDENT LIGHT

The amount of Photovoltage produced was also recorded for the composites having different concentrations of C_{60} (ranging from 2-8% by weight) at different intensities of incident light. First a cell with a composite film of certain % of C_{60} was taken and the photovoltage produced for different intensities of incident light was recorded. The cell was then replaced with another having a different concentration of C_{60}

and the photovoltage produced at different intensities of incident light was recorded. This was done for composite films having 2%, 4%, 6% and 8% C_{60} by weight. The table below shows the photovoltage produced for composites having different concentrations of C_{60} at different intensities of the incident light.

Intensity Of Incident light (mW/Sq.cm)	Photovoltage (mV)			
	Composite with 8% C_{60}	Composite with 6% C_{60}	Composite with 4% C_{60}	Composite with 2% C_{60}
3.5	110	190	162	80
6	200	290	280	130
9	210	380	430	170
12	255	420	550	210

Table 4.3 Photovoltage (average value) produced for the composites involving poly(β-pinene) and different concentrations of C_{60} at different intensities of light

4.11.3 PHOTOVOLTAGE PRODUCED FOR THE COMPOSITES HAVING DIFFERENT CONCENTRATIONS OF C_{60} USING NITROGEN LASER WITH A FIXED INCIDENT LIGHT INTENSITY

Measurements were also performed for composites having different concentrations of C_{60} using Nitrogen Laser (325nm) with a fixed incident light intensity of 2mW/sq.cm. The results are shown in the table below.

It was observed that the composite involving poly(β-pinene) and 4% C_{60} by weight showed better performance when compared to the composites involving poly(β-pinene) with other concentrations of C_{60}. This is due to the better homogeneity of the composite involving poly(β-pinene) and 4% C_{60} by weight when compared to other composites.

Sample	Photovoltage (mV)
Composite with 2% C_{60}	20
Composite with 4% C_{60}	80
Composite with 6% C_{60}	39
Composite with 8% C_{60}	18

Table 4.4 Photovoltage produced for the composites with poly(β-pinene) and different concentrations of C_{60} using Ni laser as light source

4.11.4 I-V CHARACTERISTICS

An experiment was done to study the change in current with the change in applied voltage using a Stimulus Measuring Unit (SMU) for a photovoltaic cell having a composite involving poly(β-pinene) and 8% C_{60} by weight. The intensity of the incident light was fixed at 4mW/Sq.cm. The SMU is turned ON after the photovoltaic cell is connected to it. The SMU supplies the voltage in steps and the corresponding current output is recorded. For a given supply voltage, the current produced was found to be higher when the light was incident on the cell compared to the value of current when the light was cut OFF. The following graphs show the amount of current produced corresponding different values of voltage supply in a photovoltaic cell having a composite involving poly(β-pinene) and 8% C_{60} by weight.

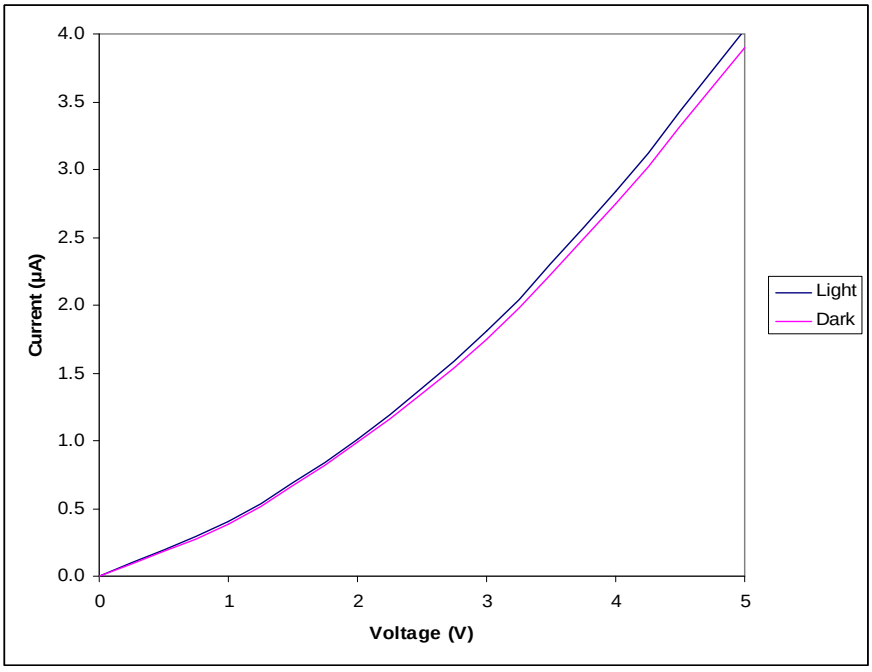


Figure 4.10 The I-V characteristics for a composite involving poly(β-pinene) and 8% C_{60} by weight

It was observed that for a light intensity of 4mW/Sq.cm and an applied voltage of 5V, a photocurrent of 0.13μA was generated for the composite involving poly(β-pinene) and 8% C_{60} by weight. Further work needs to be done to study the I-V characteristics.

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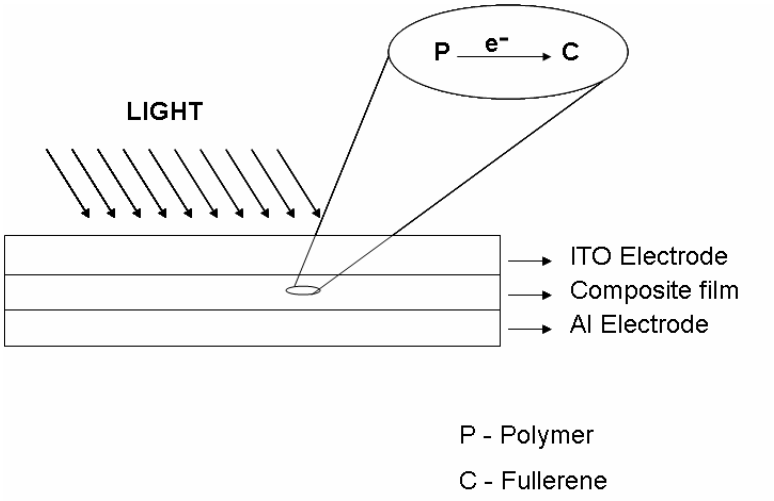
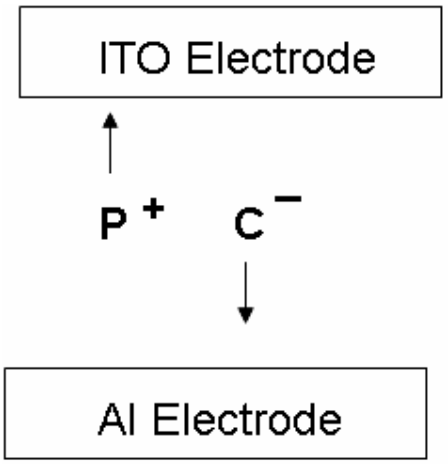
4.12 MECHANISM

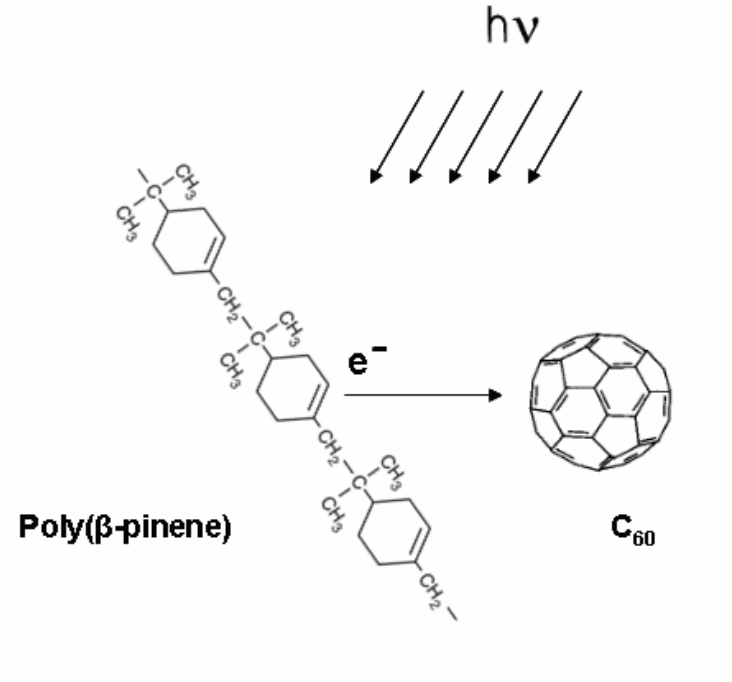
In the composite involving poly(β-pinene) and C_{60}, the polymer, poly(β-pinene) acts as an electron donor and the C_{60} acts as an electron acceptor.



(a)



(b)



(c)

Figure 4.11 Mechanism: (a) Electron transfer to C_{60} in the excited state (b) Holes transported to ITO electrode and electrons to Al electrode in the excited state (c) Excited state electron transfer from poly(β-pinene) to C_{60}

When the light is incident on the composite film, electron hole pairs are produced. From this excited state of the polymer, electron is transferred to C_{60}. The electrons are then transported to the Al electrode by the C_{60} and the holes are transported to indium tin oxide electrode. This transportation of electrons and holes produces the photovoltage.

4.13 DISCUSSION

Though the use of nonconjugated polymers in solar cells is being reported for the first time, it offers many promising advantages over the traditional solar cells using inorganic materials and the solar cells using organic conjugated polymers.

When it comes to the ease of fabrication, the photovoltaic cell formed using the composite involving a nonconjugated conducting polymer and C_{60} is very easy to fabricate when compared to the traditional inorganic solar cells whose fabrication is very intricate and requires lots of skilled labor. It is also easy when compared to the other organic solar cells which use conjugated polymers. The cells using conjugated polymers use methods like spin coating of the polymer composite to form the thin films. But here it is done at normal environmental conditions by just dropping a few drops of the polymer on the Al electrode and letting it dry. This is a very easy method when compared to the other solar cells.

When looked at the economy point of view, the photovoltaic cells using the composites involving a nonconjugated conducting polymer and C_{60} is far cheaper when compared to the inorganic solar cells.

The organic solar cells enjoy another great advantage over the inorganic solar cells. The organic solar cells can offer a very large area which is very difficult to obtain using the inorganic materials in the traditional solar cells.

The photovoltage produced in the organic solar cells using nonconjugated conducting polymers for different intensities of light proves to be good when compared with the photovoltage produced by the organic cells using the conjugated polymers. For an incident light intensity of 6 mW/ Sq.cm, the organic solar cell using the composite involving the nonconjugated conducting polymer, poly(β-pinene) and 4% C_{60} by weight produced a photovoltage of nearly 280mV which is similar to some of the organic solar cells using conjugated polymers [75, 76].

Further research needs to be carried out for studying the current characteristics of the cell. At present the thickness of the cell is one of the issues in measuring the current. The films used in these cells have a thickness in the range 1 µm to 2 µm. Cells with thinner films with thickness in the orders of few nanometers can produce a large current. But when films of thickness in the range of nanometers were produced, they had a problem of shorting. Further work needs to be done in order to overcome this problem.

CHAPTER 5

THE PHOTOVOLTAIC EFFECT IN COMPOSITE INVOLVING A NONCONJUGATED CONDUCTING POLYMER, CIS-1,4-POLY(ISOPRENE) AND BUCKMINSTERFULLERENE, C_{60}

5.1 INTRODUCTION

An effort was made to form a composite using the nonconjugated conducting polymer cis-1,4-poly(isoprene) and C_{60} and study its photovoltaic characteristics. Thin films of the composites were formed and the optical and surface characteristics were studied before the photovoltaic measurements were made. This is discussed in detail in the following sections.

5.2 PREPARATION OF THE COMPOSITE INVOLVING A NONCONJUGATED CONDUCTING POLYMER, CIS-1,4-POLY(ISOPRENE) AND C_{60}

The composite was formed by using Toluene as the base solvent. Weighed quantities of cis-1,4-poly(isoprene) and C_{60} were taken and added to it and let to dissolve to form the composite. Composites having different concentrations of cis-1,4-poly(isoprene) and C_{60} were prepared. Typically, the amount of C_{60} was measured as %

by weight in the composite. The following table shows the composites having the two different concentrations of C_{60} by % weight.

Sample	**% of C_{60} by weight in the composite**
Sample 1	8%
Sample 2	4%

Table 5.1 Composites with cis-1,4-poly(isoprene) and different concentrations of C_{60}

Once the composites were prepared they were heat treated to enhance the solubility of the solutes. Upon the formation of the composites, their optical properties, absorption spectrum and photoluminescence, were studied.

5.3 ABSORPTION SPECTRUM

Films of the composites were formed and the absorption spectra of these films were studied. Pristine cis-1,4-poly(isoprene) has an absorption peak at 280nm. The optical absorption spectra of the composites formed by cis-1,4-poly(isoprene) and C_{60} at different concentrations is shown in figure . The absorption spectra of the composites show two distinct peaks, one at 280nm and the other at 335 nm. The peak at 280 nm observed in the composite is due to cis-1,4-poly(isoprene) and C_{60}, while the peak at 335nm is due to C_{60} alone. The inset in figure shows the absorption spectrum of C_{60}.

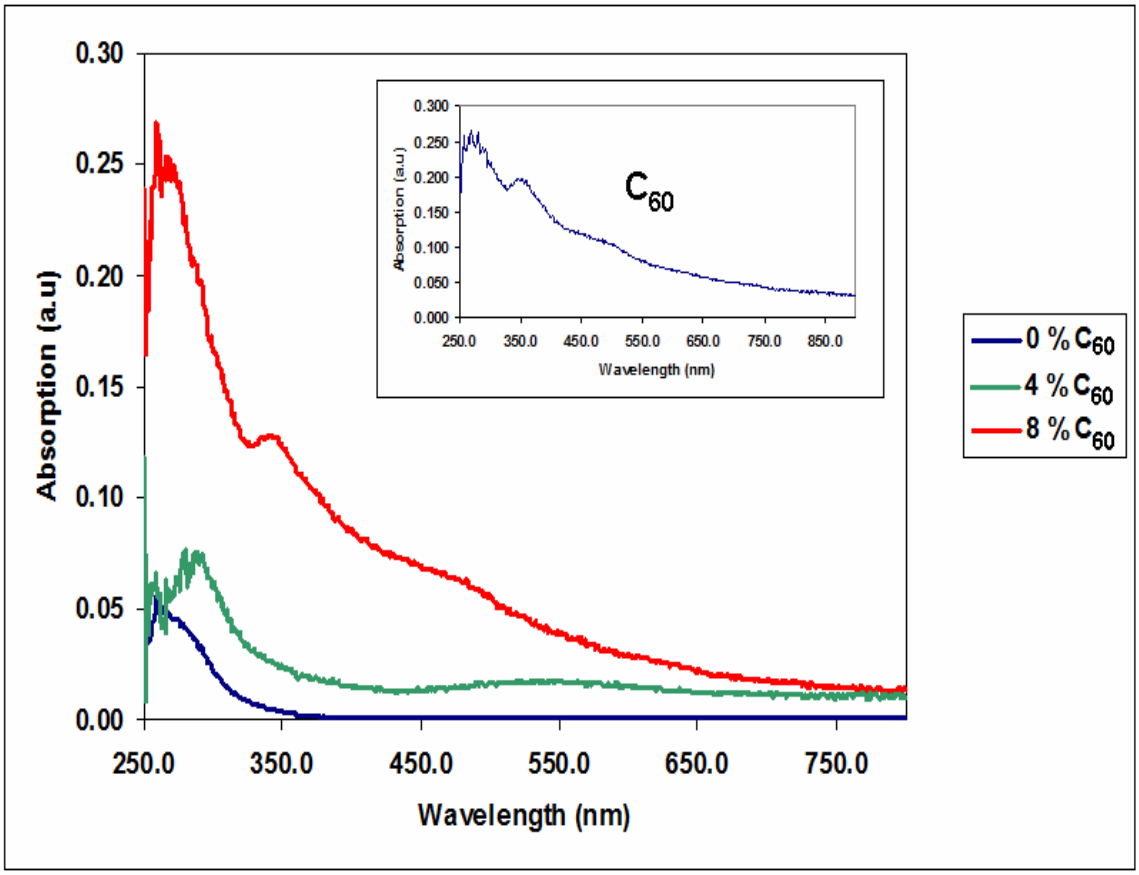


Figure 5.1 Absorption Spectra of the composites involving cis-1,4-poly(isoprene) and C_{60} (% weight)

The intensity of the absorption peak for the composite film increases with increase in the concentration of C_{60} (by % weight). In the figure, the bottom spectrum corresponds to the composite with 0% C_{60} by weight (pristine cis-1,4-poly(isoprene)). The spectrum above it in green color corresponds to the composite having 4% C_{60} by weight. The top most spectrum in red color corresponds to the composite having 8% C_{60} by weight.

5.4 PHOTOLUMINESCENCE

The photoluminescence of the composite films has been studied using Perkin Elmer LS-55 spectrometer. Pristine cis-1,4-poly(isoprene) has an emission peak at 430nm for an excitation wavelength of 280nm. The photoluminescence of the composite film involving cis-1,4-poly(isoprene) and C_{60} was studied at the same excitation wavelength of 280 nm. It was observed that the photoluminescence was quenched by a considerable amount in the composite involving cis-1,4-poly(isoprene) and C_{60} due to the transfer of electron from the polymer, cis-1,4-poly(isoprene) to C_{60} in the excited state. This is shown in the following figures.

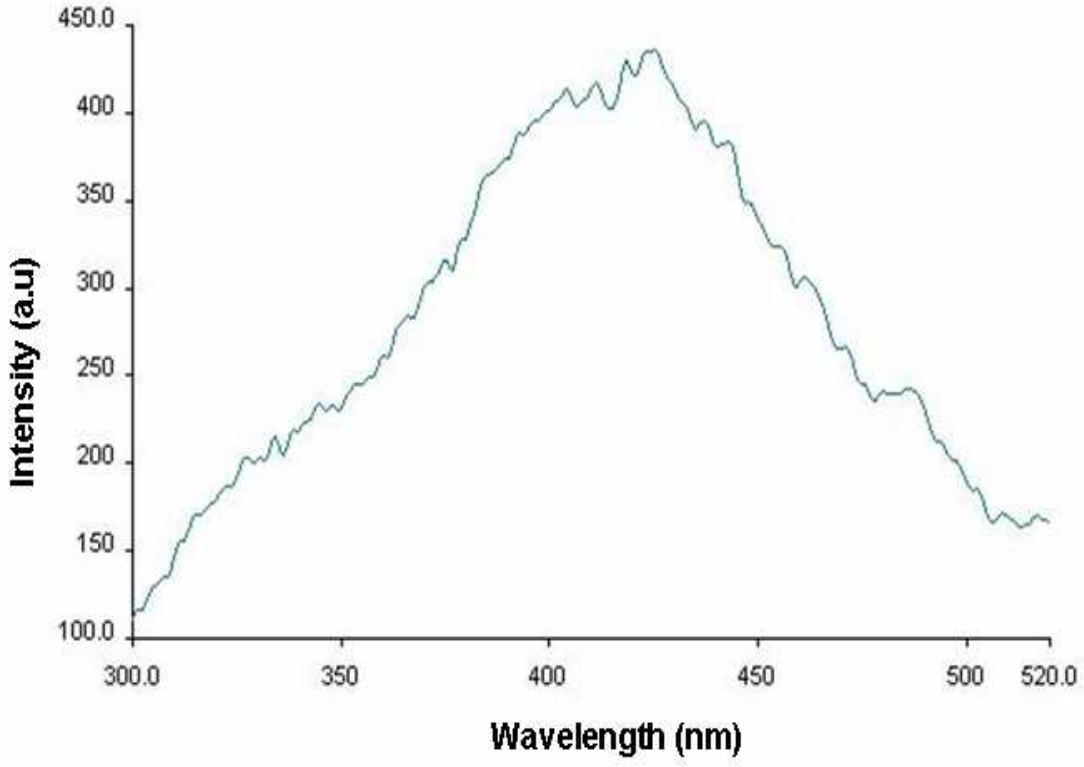


Figure 5.2 Photoluminescence spectrum of pristine cis-1,4-poly(isoprene)

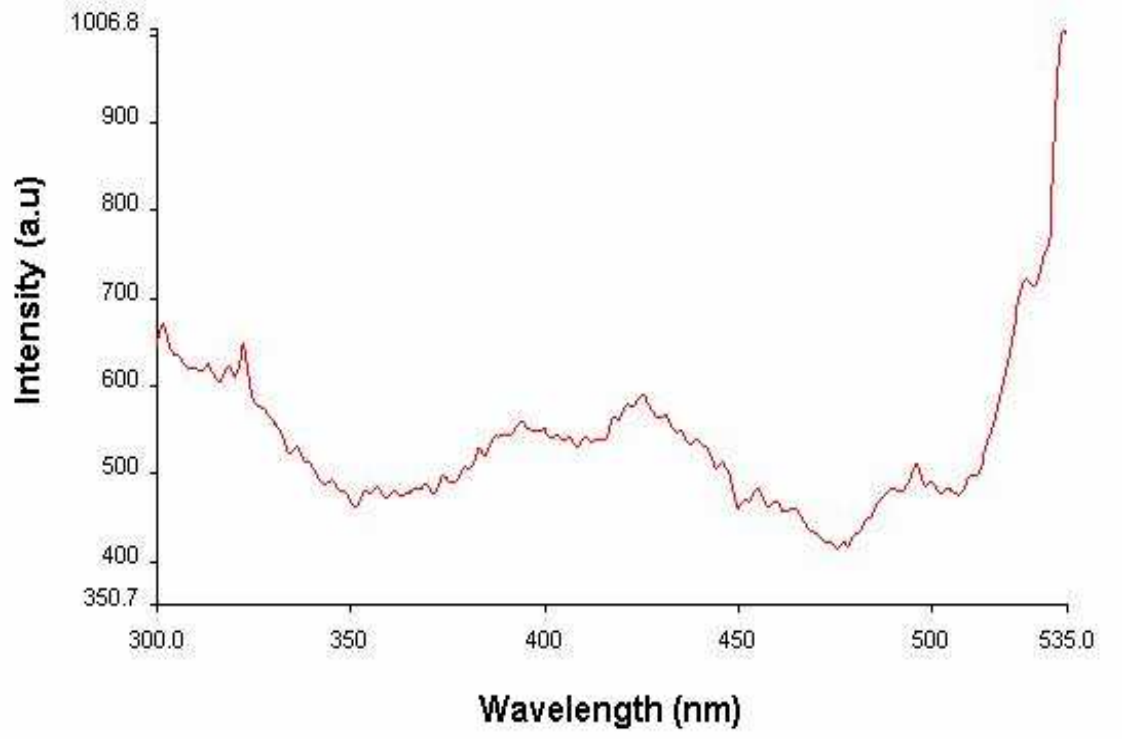
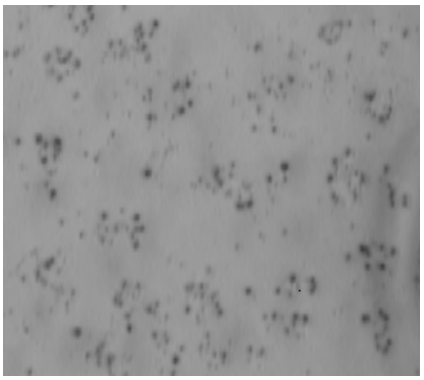


Figure 5.3 Photoluminescence of the composite involving cis-1,4-poly(isoprene) and buckminsterfullerene, C_{60}

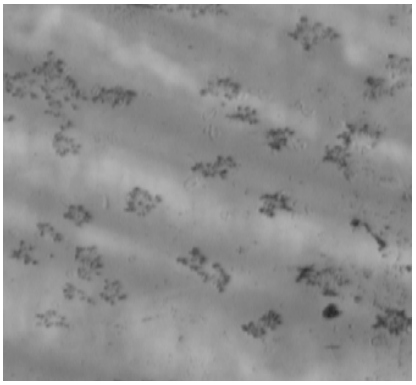
It can be observed from the figure that the photoluminescence is quenched by a considerable amount for the composite involving cis-1,4-poly(isoprene) and C_{60} at the same excitation wavelength of 280nm.

5.5 PREPARATION OF THIN FILMS OF THE COMPOSITES

Thin films of the composites involving the nonconjugated conductive polymer, cis-1,4-poly(isoprene) and C_{60} were cast on a glass slide. This was done by taking a few drops of the solution of the composite in a pipette and putting it on a glass slide. It is then allowed to dry under normal environmental conditions. The following figure shows the optical micrographs of these films.



Composite with 4% C_{60}



Composite with 8% C_{60}

Figure 5.4 Optical micrographs of the composite films involving the nonconjugated conductive polymer, cis-1,4-poly(isoprene) and C_{60}

It was observed that the composite films having cis-1,4-poly(isoprene) and C_{60} was non homogeneous compared to the films of the composite having poly(β-pinene) and C_{60}. This is because the poor solubility of cis-1,4-poly(isoprene) and C_{60} in the solution.

5.6 PREPARATION OF ELECTRODES

The electrodes used in the experiment were Indium tin oxide coated glass slide and Aluminum coated glass slide. The Indium tin oxide glass slides with specifications of 4-8Ω resistance were ordered from a vendor. The aluminum coated glass slides were prepared in the Photonic Materials Research Laboratory using the Vacuum Evaporator.

5.7 LIGHT SOURCE

The light source used in the experiment was a white light bulb manufactured by GE, Inc. The wavelength spectrum of the light source is as shown in the figure 4.6 which was measures using Ocean Optics Spectrometer USB2000. The wavelength ranges from

200 nm to 700 nm. The intensity of the light was measured using Newport Optical Power meter, model 1830-C.

5.8 ELECTROMETER

The electrical measurements were made using a high impedance electrometer manufactured by Keithley Instruments (Model: Keithley 617 Programmable Electrometer).

5.9 EXPERIMENTAL SETUP

Photovoltaic cells used in the research were formed by sandwiching the composite film between two electrodes. Aluminum coated glass slide was used as one electrode and indium tin oxide coated glass slide was used as the other electrode. The Aluminum electrode was prepared by evaporating aluminum on a glass slide using the Vacuum Evaporator.

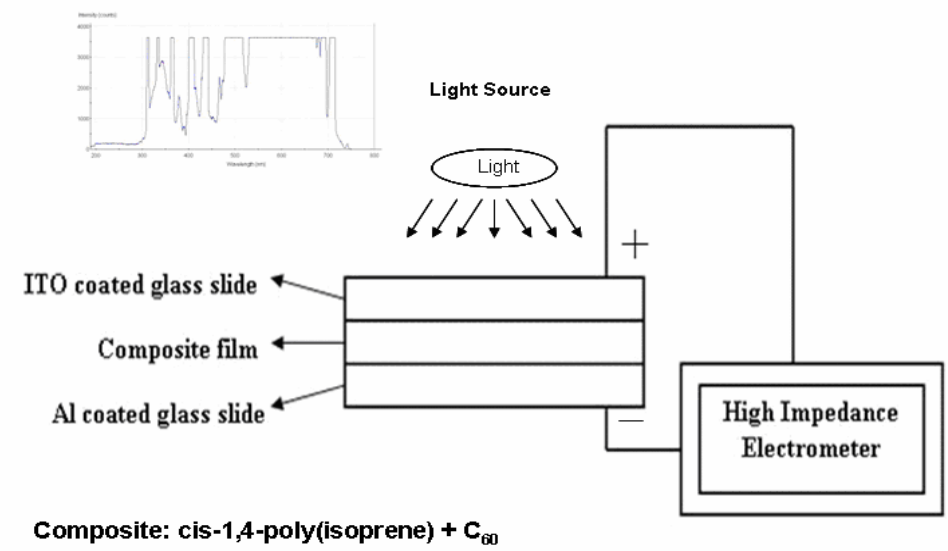


Figure 5.5 Experimental setup to measure the photovoltage for the composite involving cis-1,4-poly(isoprene) and C_{60}

The film of the composite involving cis-1,4-poly(isoprene) and C_{60} was cast on the aluminum electrode and the indium tin oxide electrode was placed on it. Pressure was applied to keep the composite and the electrodes in contact. Aluminum electrode was connected to the negative terminal of a high impedance electrometer (Keithley 617 Programmable Electrometer) and the indium tin oxide electrode was connected to the positive end of the high impedance electrometer. The Indium tin oxide electrode was placed facing up to ensure that the light is incident on the polymer through this electrode. The experimental setup is shown in figure.

The inset in the figure 5.5 shows the wavelength spectrum of the white light source used in these measurements. The intensity of the incident light is calibrated in terms of the distance of the light source from the photovoltaic cell. The distance of the light source is changed to change the intensity of the incident light.

5.10 EXPERIMENT

The sample was set on a horizontal surface and connected to the high impedance electrometer using crocodile clips. The light source was placed in such a way that the light was incident directly on the composite film through the tin oxide electrode. The distance of the light source from the sample was calibrated in terms of intensity of incident light using a power meter. Therefore by changing the distance of the light source from the sample the intensity of incident light can be changed.

Before the start of the experiment the cell was discharged for one full night to make it free of residual charges. This is done by placing the sample in short circuit

connection i.e., connecting the Al electrode and the Indium Tin Oxide electrode using a crocodile clip.

Once the setup was ready the electrometer was turned ON and it was made sure that the cell did not short. This was done by setting the electrometer in resistance mode and making sure that it showed high resistance (usually in Giga-ohms). If the cell showed high resistance, the electrometer was changed to voltage mode and the initial voltage was recorded after the reading was stable. The light source was then turned ON and the voltage reading in the electrometer was recorded. The difference in the voltage readings of the electrometer, with the light turned OFF and light turned ON, gives the amount of photovoltage produced at that particular intensity of incident light.

After this, the distance of the light source from the sample was changed to set it at a different intensity level and the experiment was repeated again. In this way the amount of photovoltage produced was recorded for different intensities of incident light source.

5.11 RESULTS

Photovoltage produced for the composite involving cis-1,4-poly(isoprene) and C_{60} was recorded at different intensities of incident light in the wavelength range of 200 nm - 700 nm.

The following table shows the photovoltage produced for the composite involving cis-1,4-poly(isoprene) and 4% of C_{60} by weight at different intensities of incident light.

Intensity of incident light (mW/Sq.cm)	Photovoltage (mV)
4	20 – 50
7	30 – 80
11	50 – 80
13	50 – 70

Table 5.2 Photovoltage produced for the composite involving cis-1,4-poly(isoprene) and 4% of C_{60} by weight at different intensities of incident light

The photovoltage produced is shown as a range because it was not consistent. It fluctuated between the boundaries of the range.

The following table shows the photovoltage produced for the composite involving cis-1,4-poly(isoprene) and 8% of C_{60} by weight at different intensities of incident light.

Intensity of incident light (mW/Sq.cm)	Photovoltage (mV)
4	30 – 60
7	50 – 80
11	70 – 90
13	70 – 80

Table 5.3 Photovoltage produced for the composite involving cis-1,4-poly(isoprene) and 8% of C_{60} by weight at different intensities of incident light

5.12 DISCUSSION

The main problem encountered here was the non homogeneity of the composite films. The photoluminescence of the composite film was quenched considerably which shows that there is a transfer of electron from the polymer to C_{60}. The reason for the photovoltage produced being less consistent can be attributed to the less homogeneity of the film. If the film homogeneity can be improved the photovoltaic cell can produce a stable and higher photovoltages.

CHAPTER 6

THE PHOTOVOLTAIC EFFECT IN COMPOSITE INVOLVING A NONCONJUGATED CONDUCTING POLYMER, STYRENE-BUTADIENE RUBBER (SBR) AND BUCKMINSTERFULLERENE, C_{60}

6.1 INTRODUCTION

An effort was made to form a composite using the nonconjugated conducting polymer SBR and C_{60} and study its photovoltaic characteristics. Thin films of the composites were formed and the optical and surface characteristics were studied before the photovoltaic measurements were made. This is discussed in detail in the following sections.

6.2 PREPARATION OF THE COMPOSITE INVOLVING A NONCONJUGATED CONDUCTING POLYMER, STYRENE-BUTADIENE RUBBER (SBR) AND C_{60}

The composite was formed by using Toluene as the base solvent. Weighed quantities of SBR and C_{60} were taken and added to it and let to dissolve to form the composite. Composites having different concentrations of SBR and C_{60} were prepared. Typically, the amount of C_{60} was measured as % by weight in the composite. The

following table shows the composites having the two different concentrations of C_{60} by % weight.

Sample	**% of C_{60} by weight in the composite**
Sample 1	6%
Sample 2	4%

Table 6.1 Composites with SBR and different concentrations of C_{60}

Once the composites were prepared they were heat treated to enhance the solubility of the solutes. Upon the formation of the composites, their optical properties, absorption spectrum and photoluminescence, were studied.

6.3 ABSORPTION SPECTRUM

Films of the composites were formed and the absorption spectra of these films were studied. Pristine SBR has an absorption peak at 280nm. The optical absorption spectra of the composites formed by SBR and C_{60} at different concentrations are shown in figure. The absorption spectra of the composites show two peaks, one at 280 nm and the other at 335 nm. The peak at 280 nm observed in the composite is due to SBR and C_{60}, while the peak (shoulder) at 335nm is due to C_{60} alone. The inset in figure shows the absorption spectrum of C_{60}.

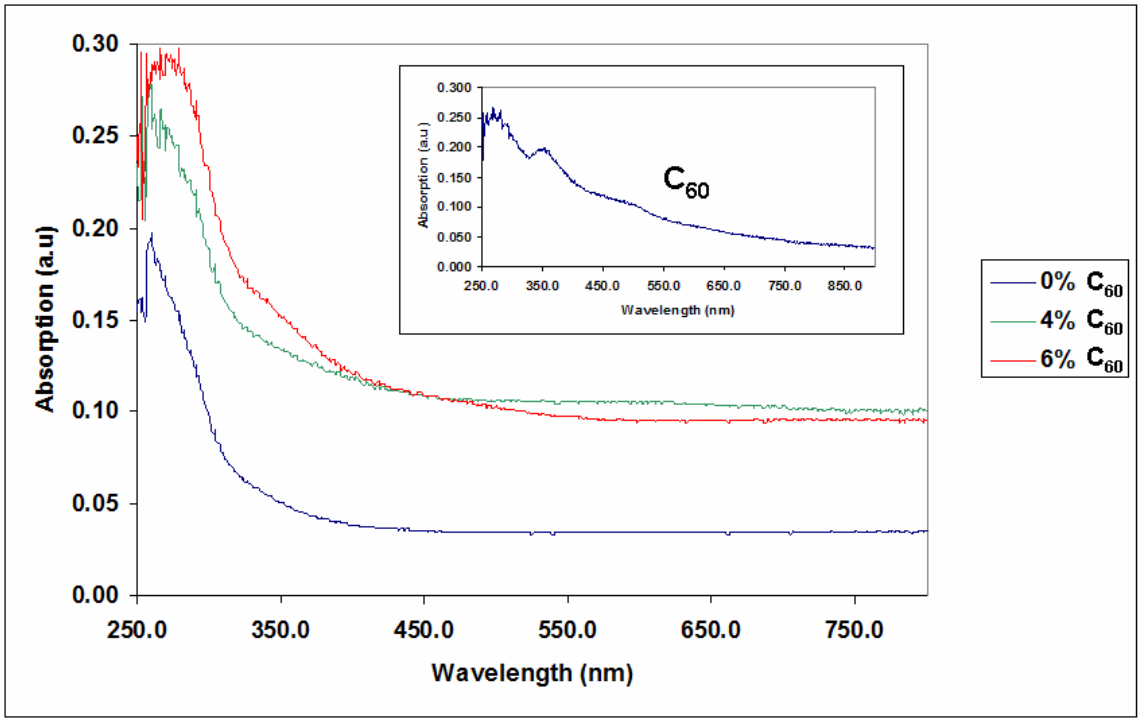


Figure 6.1 Absorption Spectra of the composites involving SBR and C_{60} (% weight)

In the figure, bottom most spectrum in blue color corresponds to the composite with 0% C_{60} by weight (pristine SBR). The spectrum above it corresponds to the composite having 4% C_{60} by weight. The top most spectrum in red color corresponds to the composite having 6% C_{60} by weight.

6.4 PHOTOLUMINESCENCE

The photoluminescence of the composite films has been studied using Perkin Elmer LS-55 spectrometer. Pristine SBR has an emission peak at 430 nm for an excitation wavelength of 280 nm. The photoluminescence of composite involving SBR and C_{60} was studied and it was observed that it was not quenched by considerable amount. The photoluminescence for pristine SBR is shown in the following figure.

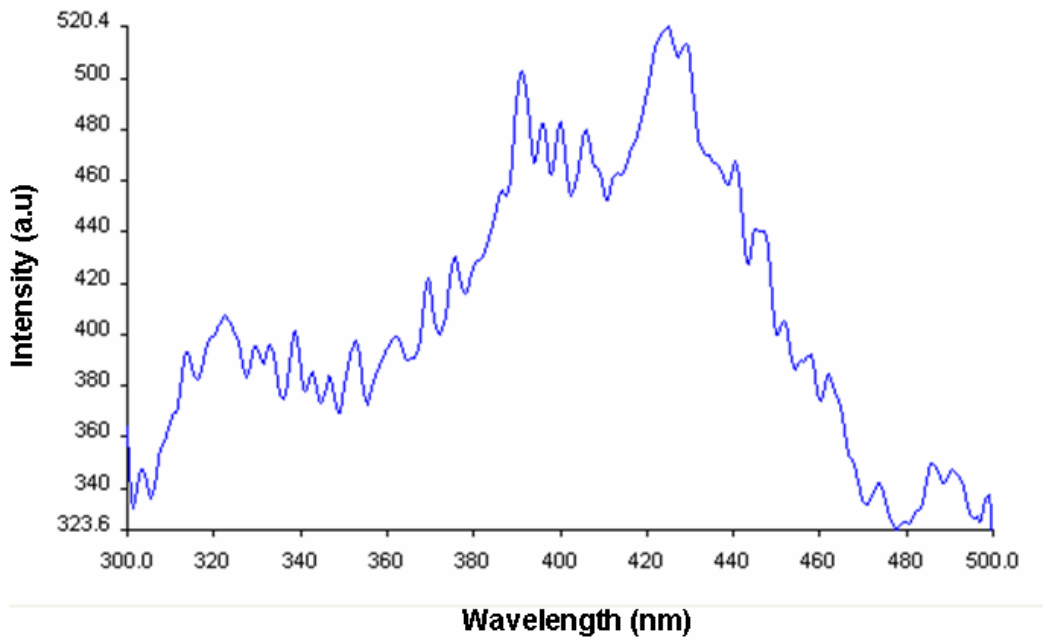


Figure 6.2 Photoluminescence spectrum of pristine SBR

The photoluminescence spectrum for the composite involving SBR and C_{60} is shown in the figure below.

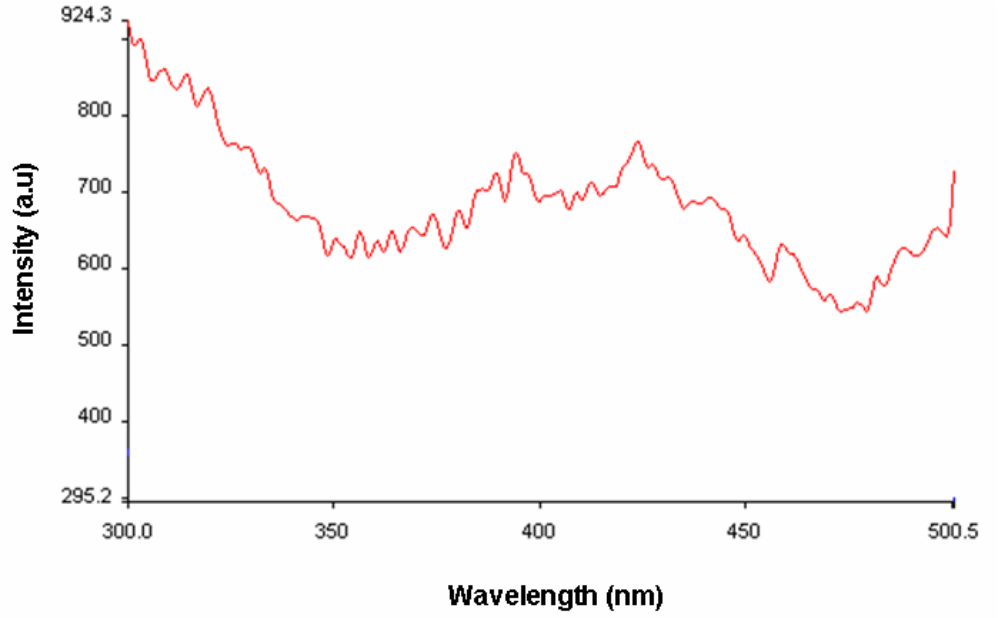
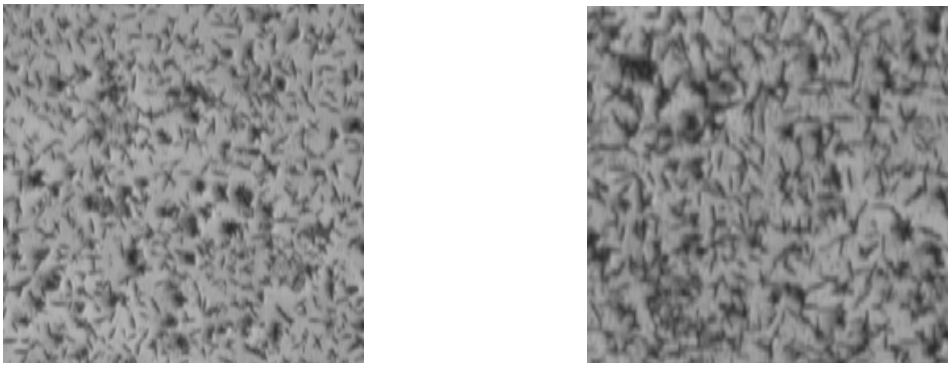


Figure 6.3 Photoluminescence of the composite involving SBR and C_{60}

6.5 PREPARATION OF THIN FILMS OF THE COMPOSITES

Thin films of the composites involving the nonconjugated conductive polymer, SBR and C_{60} were cast on a glass slide. This was done by taking a few drops of the solution of the composite in a pipette and putting it on a glass slide. It is then allowed to dry under normal environmental conditions. The following figure shows the optical micrographs of these films.



Composite with 4% C_{60} Composite with 6% C_{60}

Figure 6.4 Optical micrographs of the composite films involving the nonconjugated conductive polymer, SBR and C_{60}

It was observed that the composite films were non homogenous when compared to the films formed by the composites involving poly(β-pinene) and C_{60}. This is because of the poor solubility of the solution having SBR and C_{60}.

6.6 PREPARATION OF ELECTRODES

The electrodes used in the experiment were Indium tin oxide coated glass slide and Aluminum coated glass slide. The Indium tin oxide glass slides with specifications of 4-8Ω resistance were ordered from a vendor. The aluminum coated glass slides were prepared in the Photonic Materials Research Laboratory using the Vacuum Evaporator.

6.7 LIGHT SOURCE

The light source used in the experiment was a white light bulb manufactured by GE, Inc. The wavelength spectrum of the light source is as shown in the figure 4.6 which was measured using Ocean Optics Spectrometer USB2000. It has a wavelength range from 200 nm to 700 nm. The intensity of the light was measures using Newport Optical Power meter, model 1830-C.

6.8 ELECTROMETER

The electrical measurements were made using a high impedance electrometer manufactured by Keithley Instruments (Model: Keithley 617 Programmable Electrometer).

6.9 EXPERIMENTAL SETUP

Photovoltaic cells used in the research were formed by sandwiching the composite film between two electrodes. Aluminum coated glass slide was used as one electrode and indium tin oxide coated glass slide was used as the other electrode. The Aluminum electrode was prepared by evaporating aluminum on a glass slide using the Vacuum Evaporator. The film of the composite involving SBR and C_{60} was cast on the aluminum electrode and the indium tin oxide electrode was placed on it. Pressure was applied to keep the composite and the electrodes in contact. Aluminum electrode was connected to the negative terminal of a high impedance electrometer (Keithley 617 Programmable Electrometer) and the indium tin oxide electrode was connected to the

positive end of the high impedance electrometer. The Indium tin oxide electrode was placed facing up to ensure that the light is incident on the polymer through this electrode.

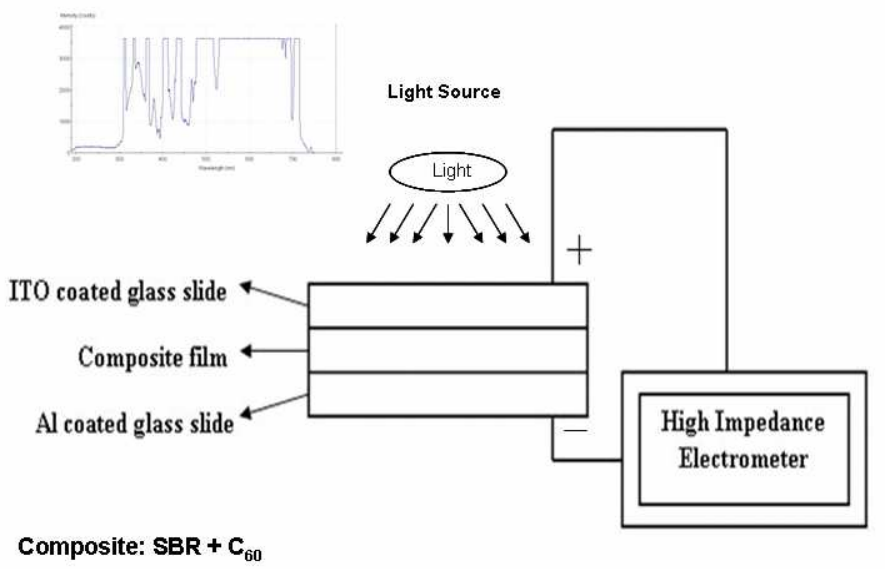


Figure 6.5 Experimental setup to measure the photovoltage of the composite involving SBR and C_{60}

The inset in the figure 6.6 shows the wavelength spectrum of the white light source used in these measurements. The intensity of the incident light is calibrated in terms of the distance of the light source from the photovoltaic cell. The distance of the light source is changed to change the intensity of the incident light.

6.10 EXPERIMENT

The sample was set on a horizontal surface and connected to the high impedance electrometer using crocodile clips. The light source was placed in such a way that the light was incident directly on the composite film through the tin oxide electrode. The

distance of the light source from the sample was calibrated in terms of intensity of incident light using a power meter. Therefore by changing the distance of the light source from the sample the intensity of incident light can be changed.

Before the start of the experiment the cell was discharged for one full night to make it free of residual charges. This is done by placing the sample in short circuit connection i.e., connecting the Al electrode and the Indium Tin Oxide electrode using a crocodile clip.

Once the setup was ready the electrometer was turned ON and it was made sure that the cell did not short. This was done by setting the electrometer in resistance mode and making sure that it showed high resistance (usually in Giga-ohms). If the cell showed high resistance, the electrometer was changed to voltage mode and the initial voltage was recorded after the reading was stable. The light source was then turned ON and the voltage reading in the electrometer was recorded. The difference in the voltage readings of the electrometer, with the light turned OFF and light turned ON, gives the amount of photovoltage produced at that particular intensity of incident light.

After this, the distance of the light source from the sample was changed to set it at a different intensity level and the experiment was repeated again. In this way the amount of photovoltage produced was recorded for different intensities of incident light source.

6.11 RESULTS

The photovoltage produced by the photovoltaic cell using the composite involving the nonconjugated polymer, SBR and C_{60} was recorded at different intensities of incident light in the wavelength range 200 nm to 700 nm.

The composite involving SBR and 6% C_{60} by weight showed little or no photovoltage produced at different intensities of incident light. Also, the composite involving SBR and 4% of C_{60} by weight showed a very little photovoltage as shown in the following table.

Intensity of incident light (mW/Sq.cm)	Photovoltage (mV)
4	10
7	15
11	25
13	8

Table 6.2 Photovoltage produced for the composite involving SBR and 4% of C_{60} by weight at different intensities of incident light

6.12 DISCUSSION

The films of the composite involving SBR and C_{60} were significantly less homogenous. Also, it was observed that the photoluminescence was not considerably quenched for the composite involving SBR and C_{60}. This means that the transfer of charges between the polymer and C_{60} was less efficient. These are the major reasons for the smaller photovoltages.

CHAPTER 7

COMPARISON OF MATERIALS BASED ON RESULTS

Composites involving nonconjugated conductive polymer and Buckminsterfullerene, C_{60} were formed for use in a photovoltaic cell. The electrical and optical properties of the composites were studied. It was observed that the composite involving poly(β-pinene) and C_{60} showed absorption peaks at 280nm and 335nm. The peak at 280nm is attributed to poly(β-pinene) and C_{60} and the peak at 335nm is attributed to C_{60} alone. The intensity of the absorption peak increased with increase in the concentration of C_{60} in the composite. The composite involving cis-1,4-poly(isoprene) and C_{60} showed absorption peaks at 280nm and 335nm. The peak at 280nm is attributed to cis-1,4-poly(isoprene) and C_{60} and the peak at 335nm is attributed to C_{60} alone. Similarly, the composite involving SBR and C_{60} showed absorption peaks at 280nm and 335nm. The peak at 280nm is attributed to cis-1,4-poly(isoprene) and C_{60} and the peak at 335nm is attributed to C_{60} alone.

In the composites formed by poly(β-pinene) and $C_{60,}$ there is a distinct peak at 335 nm. Whereas in the composite formed by cis-1,4-poly(isoprene) and C_{60} and the composite formed by SBR and C_{60} the peak at 335 nm appears to be a small shoulder.

The photoluminescence was studied for the composite involving poly(β-pinene) and C_{60} and it was found that the photoluminescence is quenched for the composite which is the result of transfer of electron from poly(β-pinene) to C_{60} in the excited state. The photoluminescence was quenched by a considerable amount for the composite involving cis-1,4-poly(isoprene) and C_{60}. The photoluminescence of the composite involving SBR and C_{60} was not quenched considerably. This can be attributed to the in homogeneity of the films.

Thin films of these composites involving nonconjugated conductive polymer and C_{60} were formed and were used in a photovoltaic cell. The surface characteristics of these films were studied. It was observed that the thin film of the composite involving poly(β-pinene) and 4% C_{60} by weight was more homogenous compared to the thin film of the composite involving poly(β-pinene) and 8% C_{60} by weight. This was due to the decrease in the solubility C_{60} in the composite above 4%. It was observed that the films of the composite involving cis-1,4-poly(isoprene) and C_{60} and the composite involving SBR and C_{60} were not homogenous due to the poor solubility of C_{60} in the composite.

The Photovoltaic cells were formed using the thin films of the composites with various concentrations of C_{60}. The photovoltaic characteristics of these cells were studied.

It was observed that the composite involving poly(β-pinene) and C_{60} produced better photovoltage compared to the composite involving cis-1,4-poly(isoprene) and C_{60} and the one involving SBR and C_{60}. This can be attributed to the less homogenous nature

of the former two composites when compared with the one involving poly(β-pinene) and C_{60}.

The photovoltage measurements were made for the composites involving poly(β-pinene) and various concentrations of C_{60} as a function of intensity of light using the white light source with a wavelength range from 200 to 700nm. It was observed that the composite involving poly(β-pinene) and 4% of C_{60} by weight exhibited better results compared to the composites involving poly(β-pinene) and other concentrations of C_{60}. The photovoltage produced for the composite involving poly(β-pinene) and 4% of C_{60} by weight showed a linear dependence on intensity of incident light. A light intensity of 6mw/sq.cm yielded a photovoltage of 280mV for the composite involving poly(β-pinene) and 4% of C_{60} by weight.

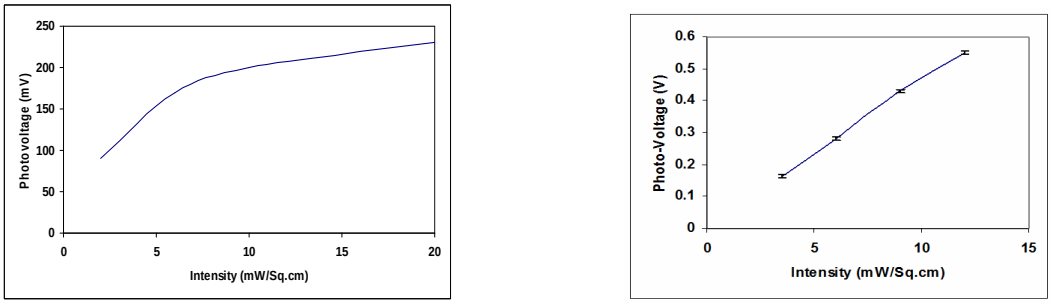
Also, the photovoltage measurements were made for the composites involving poly(β-pinene) and C_{60} as a function of the concentration of C_{60} at a fixed light intensity of 2mW/sq.cm using Nitrogen Laser (325nm). It was observed that the composite involving poly(β-pinene) and 4% of C_{60} by weight produced a better photovoltage in comparison with the composite having poly(β-pinene) and other concentrations of C_{60}. This is because the composite involving poly(β-pinene) and 4% of C_{60} by weight was more homogenous compared to the others.

Also a few current vs. voltage measurements were made on the composite involving poly(β-pinene) and 8% of C_{60} by weight. The current measurements could not be done due to the problem of shorting of the cell when thin films of the composites with thickness in the range of nanometers were used in the cells.

These photovoltaic cells formed by the organic nonconjugated conductive polymers and C_{60} had many advantages over the traditional inorganic solar cells like

- Possibility of achieving extremely high optical absorption coefficient
- Can produce very thin solar cells which enable the use of very small amount of the material
- Can produce large area solar cells which is a major drawback in inorganic solar cells
- Ease of fabrication
- Less maintenance
- Significantly cheaper compared to the traditional solar cells
- Involves low temperature processes in manufacturing when compared to that of inorganic solar cells

Also when compared to the organic photovoltaic cells formed by conjugated conductive polymers and molecular systems [75, 76], these cells showed comparable or higher photovoltages.



(a) (b)

Figure 7.1 Photovoltage vs. incident light intensity for a composite involving (a) copper phthalocyanine (CuPc)/PTCBI [75, 76] (b) poly(β-pinene) and 4% C_{60} by weight

It can be seen that the photovoltage produced by the photovoltaic cell involving a conjugated system CuPc and 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI) [75, 76] is comparable to the photovoltaic cell involving poly(β-pinene) and 4% C_{60} by weight.

The nonconjugated conductive polymers are significantly cheaper than conjugated conductive polymers. More work needs to be done in the current and efficiency measurements for these cells.

The results we have for the composite involving poly(β-pinene) and 4% of C_{60} by weight show that these are highly promising for applications as low cost photodetectors. The present day photodetectors use inorganic materials like silicon, germanium, cadmium sulphide, indium gallium arsenide, lead sulphide, etc. But the nonconjugated conductive polymers are far cheaper when compared to these materials which enable us to produce lower cost photodetectors. Also when compared to the conjugated conductive polymers, the nonconjugated conductive polymers are more easily processable. This gives the nonconjugated conductive polymers an edge over conjugated conductive polymers for the production of low cost photodetectors.

In the future, further work needs to be done to produce the composite films with thickness in the range of a few nanometers, to enhance the current produced. Also, work needs to be done in the area of current and efficiency measurements.

Also, more photovoltaic measurements are to be made using the composites formed by the nonconjugated polymers cis-1,4-poly(isoprene) and SBR and C_{60}. Work needs to be done increase the homogeneity of these composite films in order to produce better photovoltage.

CHAPTER 8

SUMMARY

The photovoltaic effect in a composite involving nonconjugated conducting polymer and C_{60} has been studied. Composite involving a nonconjugated conductive polymer such as poly(β-pinene), cis-1,4-poly(isoprene) and SBR, and C_{60} was formed for use in a photovoltaic cell. The optical absorption and photoluminescence spectra of the films of these composites were studied. When the composites were formed, it was observed that the photoluminescence was totally quenched for the composite involving poly(β-pinene) and C_{60} and considerably decreased for the composite involving cis-1,4-poly(isoprene) and C_{60}. The composite involving SBR and C_{60} did not show as much quenching of photoluminescence.

It was observed that the composite involving poly(β-pinene) and C_{60} produced better photovoltaic characteristics when compared to the other composites. Among the composites formed by poly(β-pinene) and C_{60}, the one having 4% of C_{60} by weight showed the best performance. This can be attributed to the excellent homogeneity of the composite film at this concentration. The photovoltage produced for the composite involving poly(β-pinene) and 4% C_{60} by weight was linearly dependent on light intensity.

About 280 mV was generated for an intensity of ~ 6mW/sq.cm. Pristine poly(β-pinene) has a photoluminescence peak at 360 nm for excitation at 280 nm. This photoluminescence was quenched when C_{60} was added to form the composite with poly(β-pinene). Therefore, the photovoltaic effect appears to be a result of excited state electron transfer from poly(β-pinene) to C_{60}.

The photovoltaic measurements of the composite involving poly(β-pinene) and C_{60} show that these are highly promising for application in low cost photodetectors and photo-sensors when compared to traditional photodetectors. Additional applications will include low cost solar cells.

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